it is assumed that Os^{II} is the only appreciable light absorber at 460 nm. The approximation in eq A2 is valid for optically dilute solutions.

The quenching quantum yield is given by eq A3. In eq A3,

$$\phi_q = \left[\frac{k_q[Q]}{k_q[Q] + 1/\tau}\right] \quad (A3)$$

k_q is the quenching rate constant for quencher Q and τ is the lifetime with no added quencher. Incorporating the relationships in eqs A2 and A3 into eq A1 and integrating from time = 0 to t gives eq A4. Substitution of the relationships $[Os^{II*}]_t = C(I_t - I_\infty)$ and $[Os^{II*}]_{t=0} = C(I_0 - I_\infty)$ into eq A4 provides the basis

$$\ln\left[\frac{[Os^{II}]_t}{[Os^{II}]_{t=0}}\right] = -kt = -2.303 I_0 \epsilon b \phi_q t = -2.303 I_0 \epsilon b \left[\frac{k_q[Q]}{k_q[Q] + 1/\tau}\right] t \quad (A4)$$

for the plot in Figure 5 and leads to the expression for the slope in eq 10. In eq A4, I_0, I_t, and I_∞ are the emitted light intensities at times 0, t, and ∞, and C is a constant.

Synthesis of Octamethylferrocene Derivatives via Reaction of (Octamethylferrocenyl)methyl Carbocation with Nucleophiles and Application to Functionalization of Surfaces

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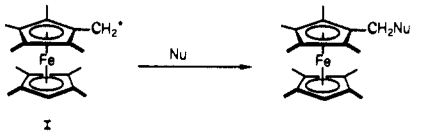
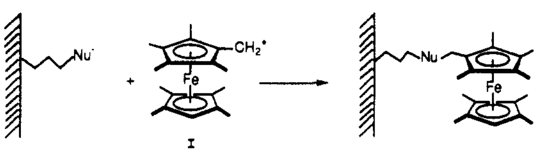
Abstract: Formylation of octamethylferrocene, $Fe(C_5Me_4H)_2$, using *N,N'*-dimethylformamide/$OPCl_3$ in $CHCl_3$ solvent at 60–70 °C gives octamethylformylferrocene in high yield (~95%). The aldehyde can be converted to a CN group to give octamethylcyanoferrocene or can be used to prepare ethyl β-(octamethylferrocenyl)acrylate. Most important, reductionn of octamethylformylferrocene using $LiAlH_4$ in Et_2O yields the alcohol in ~95% yield. Acid-catalyzed (HBF_4) dehydration of the alcohol, III, leads to formation of (octamethylferrocenyl)methyl carbocation in almost quantitative yield. The carbocation I can be isolated as an orange-red BF_4^- salt in ~90% yield from octamethylferrocene. I shows sharp ^{13}C and ^1H NMR spectral features consistent with formulation as a diamagnetic Fe(II) species with the positive charge localized on the C having two H's. I slowly dimerizes, even in the solid state, to a C–C coupled product with two Fe(III) centers. The paramagnetic, blue-green dimer can be reduced with cobaltocene or aqueous $Na_2S_2O_4$ to 1,2-bis(octamethylferrocenyl)ethane. Reaction of (octamethylferrocenyl)methyl carbocation with nucleophiles is a convenient synthetic route to octamethylferrocene derivatives, which have proved difficult to obtain by electrophilic substitution of octamethylferrocene. Reaction of the new carbocation I has been used to synthesize octamethylferrocenyl derivatives in good to excellent yields (~60–95%) via reaction with amines, thiols, or CN^-. Reaction of (octamethylferrocenyl)methyl carbocation with surface-confined nucleophiles such as NH_2 or SH [surfaces derivatized with $(MeO)_3Si(CH_2)_3NH_2$ or $(MeO)_3Si(CH_2)_3SH$] is a convenient way to attach octamethylferrocene derivatives to surfaces including SiO_2, Pt, and indium tin oxide (ITO).

We report the synthesis of octamethylferrocene derivatives via nucleophilic attack on the carbocation represented by I, eq 1, and the reaction of I with surface-confined nucleophiles, eq 2. The synthesis, structure, and reactivity of a variety of ferrocene derivatives has been well documented over the past 30 years,[1] including detailed studies of ferrocenylmethyl carbocations.[2] However, polymethylferrocene derivatives having transformable functional groups have been relatively unexplored.



I

(1)



I

(2)

We are interested in using polymethylferrocene reagents as electrode surface modifiers. The chemistry represented by eq 2 is a new way to derivatize surfaces with a durable, redox-active molecule that may be of importance in electrocatalysis.[3] For example, it has demonstrated that electrode surfaces derivatized with a pentamethylferrocene derivative give a nearly reversible response to cytochrome *c*.[3f] For mediated oxidation and reduction of cytochrome *c* the potential of ferrocene itself is far too positive to be a reversible mediator. More recently we have used a ferrocene group as a labeling "tag" to study the surface coordination

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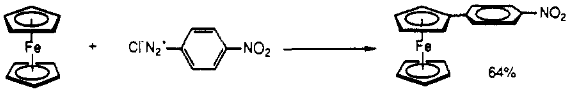
chemistry of the isonitrile group.[4] In such studies the ferrocene group enables convenient, quantitative detection of surface-bound species using electrochemical methods. The desire for ferrocene-based surface derivatizing reagents having a redox potential more negative than that of ferrocene has prompted us to synthesize a series of octamethylferrocene derivatives. Due to the electron-donating nature of methyl groups, methyl-substituted ferrocenes exhibit redox potentials more negative than that of unsubstituted ferrocene.[5] From the literature,[6] each methyl group introduced onto the rings of ferrocene can be expected to shift the $E_{1/2}$ value negative by ~50 mV. The following comparison is illustrative: $E_{1/2}$ (ferrocenium/ferrocene) = +0.41 V vs SCE while $E_{1/2}$ (decamethylferrocenium/decamethylferrocene) = −0.12 V vs SCE in CH_3CN/0.1 M $[n\text{-}Bu_4N]BF_4$.

There have been two main synthetic routes to substituted ferrocenes: electrophilic substitution at the cyclopentadienyl ring, or metalation and subsequent reaction with other electrophiles.[1] Metalated ferrocenes exhibit both reducing and nucleophilic character; hence many functional groups are not tolerated. Electrophilic substitution reactions have been used very successfully for the synthesis of ferrocene derivatives, but for octamethylferrocene, most electrophilic substitution reactions fail as a result of its reducing ability ($E_{1/2}$ = +0.01 V vs SCE in CH_3CN/0.1 M $[n\text{-}Bu_4N]PF_6$).[7a] Under standard Friedel–Crafts conditions octamethylferrocene undergoes oxidation to the unreactive octamethylferrocenium cation or decomposes oxidatively, resulting in extremely low yields of the desired product. For example, we find that acylation of octamethylferrocene with 4-chlorobutyryl chloride/$AlCl_3$ gives low yield of 1,1′-bis(4-chlorobutyryl)octamethylferrocene, eq 3, whereas ferrocene under the same conditions gives a much higher yield of 1,1′-bis(chlorobutyryl)ferrocene,[7a] eq 4.

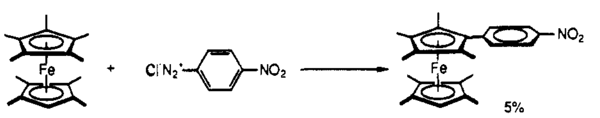
$$\text{octamethylferrocene} + Cl(CH_2)_3COCl/AlCl_3 \rightarrow \underset{\sim 5\%}{\text{1,1}'\text{-bis(chlorobutyryl)octamethylferrocene}} \quad (3)$$

$$\text{ferrocene} + Cl(CH_2)_3COCl/AlCl_3 \rightarrow \underset{65\%}{\text{1,1}'\text{-bis(chlorobutyryl)ferrocene}} \quad (4)$$

The eight methyl substituents on the cyclopentadienyl rings of octamethylferrocene can pose a problem to electrophilic substitution. For example, arylations of ferrocene with a variety of diazonium salts proceed in fair yields,[8] as we find for the reaction shown in eq 5. However, only very small amounts of product can be isolated from our attempted arylation of octamethylferrocene by azotized *p*-nitroaniline under similar conditions, eq 6.[7a] In this case octamethylferrocenium is the major product along with some decomposition of starting octamethylferrocene, as might be expected considering the reducing power of the octamethylferrocene. Such redox chemistry is already known for ferrocene itself,[9] eq 7. Further, in such electrophilic processes with octamethylferrocene, reaction at the positions having a methyl substituent may result in an η^4-coordinated ferrocene arenium ion,[10] eq 8. Instead of proceeding to lose a methyl cation to form the substitution product (eq 8), this species would likely undergo rapid intramolecular electron transfer and further decomposition. Thus, electrophilic substitution on polymethylated ferrocenes is not a desirable route to synthesize polymethylferrocene derivatives with most electrophiles.

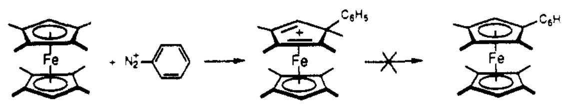


(5)



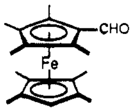
(6)

$$\text{ferrocene} + (C_6H_5)N_2^+ \rightarrow \text{ferrocenium} + N_2 + C_6H_5^{\bullet} \quad (7)$$



(8)

An important exception to the generalization regarding electrophilic substitution of octamethylferrocene concerns the use of bulky electrophiles leading to reaction at the cyclopentadienyl carbon bearing only a hydrogen. Our synthesis of I first involves preparation of the formyl species II via electrophilic chemistry (*Vilsmeier* reaction)[11] on octamethylferrocene. II is a new compound and can be used to prepare octamethylferrocene derivatives. In our work reported here we demonstrate a few examples of syntheses using II, including the preparation of I.



II

The class of reactions represented by eq 1 has not been used extensively to prepare ferrocene derivatives, despite considerable knowledge concerning ferrocenylmethyl carbocations.[2] The lack of useful syntheses via the ferrocenylmethyl carbocations is probably due to the high reactivity of the intermediate carbocation involved and the cumbersome synthesis of carbinol precursors. Allenmark synthesized ferrocene derivatives by reaction of ferrocenylmethyl carbocations with amines, ammonia, and sodium cyanide.[12] The reactions of ferrocenylmethyl carbocation with pyridine or pyridine derivatives to generate pyridinium cations have also been reported.[13] More recently, reactions between various ferrocenylmethyl carbocation derivatives and C,[14a] S[14b], and P[14c] donor nucleophiles have appeared. Similar functionalization of a related (arene)$Cr(CO)_3$-based carbocation system by reaction with nucleophiles has been reported.[15] In our work we have developed a good synthesis of the carbocation I and have been able to isolate I in good yield (~90% from octamethylferrocene) at room temperature. I is useful in subsequent synthesis according to eq 1 to prepare octamethylferrocene derivatives in good to excellent yields (~60–95%).

Experimental Section

Equipment. Solution NMR spectra were measured on Bruker WM250 (^1H 250 MHz), Varian 300 (^1H 300 MHz, ^{13}C 75.5 MHz), or Gemini 300 (^1H 300 MHz, ^{13}C 77.5 MHz) spectrometer. Solid-state CP/MAS NMR was measured with a Chemagnetics CMC-200 spec-

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trometer (^{13}C, 50 MHz). FTIR spectra were measured on a Nicolet 60SX spectrometer. Cyclic voltammetry measurements were carried out using a Pine Instruments RDE-4 bipotentiostat and a Kipp and Zonen BD 91 X-Y-Y′ recorder. A PDC-32G plasma cleaner from Harrick Scientific Corp. was used for oxygen plasma cleaning of electrodes.

Chemicals and Syntheses. Solvents were distilled from either CaH_2 (hexanes), $LiAlH_4$ [C_6H_6, tetrahydrofuran (THF), Et_2O], or P_2O_5 ($CHCl_3$). Phosphorus oxytrichloride was distilled under Ar prior to use. Acetone was dried over 3-Å molecular sieves. $(MeO)_3Si(CH_2)_3NH_2$ and $(MeO)_3Si(CH_2)_3SH$ were purchased from Petrarch and were vacuum distilled before use. All other reagents and starting materials were used as received. Elemental analyses were obtained from Galbraith Laboratories at Knoxville, TN. All syntheses of air-sensitive compounds were carried out on a Schlenk line or in a Vacuum Atmospheres drybox under Ar.

2,3,4,5-Tetramethyl-2-cyclopentenone[16] used in the synthesis of octamethylferrocene and **octamethylferrocene**[17] were prepared by the published procedures.

Octamethylformylferrocene (II). The formylation of octamethylferrocene was achieved by a slight modification of the *Vilsmeier* reaction.[11] A 250-mL round-bottom flask equipped with an Ar inlet, condenser, rubber septum, and magnetic stirring bar was charged with 4 g of octamethylferrocene (13.4 mmol) and 100 mL of dry $CHCl_3$. After the flask was flushed with Ar, 6 mL of *N,N′*-dimethylformamide (78 mmol) and 10 mL of phosphorus oxytrichloride (0.11 mol) were added through the septum. The resultant dark-purple solution was heated at 50–60 °C by using an oil bath for 6 h. After being cooled to room temperature, the solution was poured into water (400 mL) and was stirred for 30 min. This mixture was extracted with Et_2O (250 mL) three times. The combined ethereal solution was washed with water twice and then with saturated NaCl solution and was dried over Na_2SO_4. Evaporation of solvents under vacuum gave II as an orange-red, crystalline solid in 95% isolated yield, mp 235 °C. ^1H NMR ($CDCl_3$): δ 10.03 (s, 1 H), 3.42 (s, 1 H), 2.01 (s, 6 H), 1.81 (s, 6 H), 1.67 (s, 6 H), 1.63 (s, 6 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 195.5, 86.3, 83.1, 81.8, 72.8, 71.3, 70.6, 11.0, 9.8, 9.5, 9.2. Anal. Calcd (Found): C, 69.95 (70.10); H, 8.03 (8.08). The formylation of octamethylferrocene using the same procedure has also been executed on the 10-g scale with similar yields.

(Octamethylferrocenyl)methanol (III). 2 g of II (7 mmol) and 100 mL of anhydrous Et_2O were added to a 250-mL round-bottom flask, which was fitted with a condenser, Ar inlet, addition funnel, and magnetic stirring bar. A mixture of 0.15 g of $LiAlH_4$ in anhydrous Et_2O (80 mL) was then added dropwise via the addition funnel while the system was purged with a slow stream of Ar. The addition was discontinued when the color of the reaction mixture changed from orange-red to yellow (addition of excess $LiAlH_4$ results in decomposition of the product), and the mixture was stirred at room temperature for an additional 30 min. A solution of NH_4Cl (2 g) in H_2O (20 mL) was then slowly added to the above mixture. The Et_2O layer was separated, washed with H_2O and saturated aqueous NaCl, and dried over Na_2SO_4. Evaporation of solvent on a rotary evaporator gave III as a yellow crystalline solid in 95% isolated yield, mp 181 °C. ^1H NMR (C_6D_6): δ 4.29 (d, 2 H), 3.18 (s, 1 H), 1.72 (s, 6 H), 1.63 (s, 6 H), 1.62 (s, 6 H), 1.54 (s, 6 H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 81.5, 80.4, 80.2, 79.7, 70.9, 70.6, 58.0, 11.6, 9.9, 9.7, 9.6. Anal. Calcd (Found): C, 69.52 (69.27); H, 8.60 (8.63).

[(Octamethylferrocenyl)methyl carbocation]BF_4^- (I). To a solution of III (1.0 g, 3 mmol) in Et_2O (30 mL) under Ar was added 0.5 mL of acetic anhydride. A solution of 0.8 mL of $HBF_4 \cdot Et_2O$ (85%, Aldrich) was then added. An orange-red precipitate was formed immediately. The solvent was removed by filtration under Ar, and the solid was washed with Et_2O (100 mL) and pentane (50 mL) and dried under vacuum to give an essentially quantitative yield of I as the orange-red BF_4^- salt. I is moisture sensitive and was typically used immediately in subsequent reactions. UV–vis absorbances for I in CH_2Cl_2 are at 230 (ϵ = 10600), 280 (ϵ = 10000), and 480 nm (ϵ = 170). Freshly prepared samples of I show sharp ^1H and ^{13}C NMR resonances. ^1H NMR ($CDCl_3$/acetone-d_6 2:1): δ 5.27 (s, 2 H), 4.31 (s, 1 H), 1.77 (s, 6 H), 1.42 (s, 6 H), 1.32 (s, 6 H), 1.11 (s, 6 H). ^{13}C NMR ($CDCl_3$/acetone-d_6 2:1): δ 106.8, 106.4, 94.5, 93.5, 92.6, 89.4, 82.3, 9.61, 9.43, 8.97, 6.62. Upon standing in H_2O-free NMR solvents the ^1H NMR resonances slowly broaden. The eventual product is a dimer via *C–C* bond formation with the octamethylferrocenyl unit bearing the positive charges to give 1,2-bis(octamethylferroceniumyl)ethane.

Reduction of 1,2-Bis(octamethylferroceniumyl)ethane. The greenish powder of the [1,2-bis(octamethylferrocenium)ethane]$[BF_4^-]_2$ salt (0.25 g, 0.31 mmol) was dissolved in 50 mL of dry CH_2Cl_2. Cobaltocene (0.1 g, 0.5 mmol) was then added to the solution and the mixture stirred for 5 min. The solvent was removed under vacuum and the product isolated by chromatography. Elution with THF gave 1,2-bis(octamethylferrocenyl)ethane (VI) as an orange-yellow solid (60% yield), mp >280 °C dec. ^1H NMR ($CDCl_3$): δ 3.15 (s, 2 H), 2.12 (s, 4 H), 1.74 (s, 6 H), 1.71 (s, 6 H), 1.66 (s, 6 H), 1.61 (s, 6 H). ^{13}C NMR ($CDCl_3$): δ 83.3, 80.1, 79.8, 79.2, 78.7, 70.7, 26.9, 11.2, 9.9, 9.7, 9.3. Anal. Calcd (Found): C, 73.31 (73.35); H, 8.74 (8.87). The ferrocenium species can also be reduced by using aqueous $Na_2S_2O_4$.

β-(Octamethylferrocenyl)acrylate (IV). A 250-mL round-bottom flask was charged with 2 g of II (6.1 mmol), 5 g of Zn powder (pretreated with 2 M HCl, H_2O, acetone, and Et_2O and dried), and a few crystals of I_2. Dry C_6H_6 (100 mL) was then added to the flask, and the flask was equipped with a condenser, Ar inlet, and rubber septum. $BrCH_2COOEt$ (2 g, 12 mmol) was added to the reaction flask through the septum, and the mixture was refluxed with stirring for 24 h. The reaction mixture was allowed to cool to room temperature and filtered. The resulting solution was washed with saturated $Na_2S_2O_3$ solution, H_2O, and saturated aqueous NaCl and dried with Na_2SO_4. The solvent was removed by rotary evaporation, and the oily residue was chromatographed on an activated Al_2O_3 column (3 cm × 12 cm). Elution with Et_2O gave first a red band, identified to be the product, and second a purple band, which contains unreacted II. Evaporation of the solvent in vacuo gave IV as a red, crystalline solid in 90% isolated yield, mp 59 °C. ^1H NMR ($CDCl_3$): δ 7.60 (d, *J* = 16.1 Hz, 1 H), 6.03 (d, *J* = 16.1 Hz, 1 H), 4.21 (q, 2 H), 3.29 (s, 1 H), 1.92 (s, 6 H), 1.80 (s, 6 H), 1.66 (s, 6 H), 1.60 (s, 6 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 168.0, 146.4, 113.6, 84.2, 81.5, 81.3, 73.9, 71.7, 59.9, 14.4, 11.0, 10.9, 9.8, 9.1. Anal. Calcd (Found): C, 69.70 (69.92); H, 8.14 (8.25).

Octamethylcyanoferrocene (V). We used a published procedure for conversion of aldehydes to nitriles.[18] The crude product was purified by chromatography on an activated Al_2O_3 column (3 cm × 8 cm) using Et_2O as an eluant. V was obtained as a yellow, crystalline solid in 35% yield, mp 210 °C. IR ($CHCl_2$): ν_{CN} 2211 cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.42 (s, 1 H), 1.90 (s, 6 H), 1.75 (s, 6 H), 1.74 (s, 6 H), 1.69 (s, 6 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 120.5, 83.0, 82.9, 81.5, 71.9, 10.6, 10.4, 9.7, 8.8. Anal. Calcd (Found): C, 70.59 (70.23); H, 7.80 (7.83); N, 4.33 (4.10).

Octamethyl(cyanomethyl)ferrocene (VII). Freshly prepared I (1.0 g, 2.5 mmol) was shaken with a solution of NaCN (3 g) in H_2O (100 mL). The reaction was deemed complete when all of the solid I was converted to a yellow suspension. The reaction mixture was extracted with Et_2O. The ethereal solution was washed with H_2O and saturated aqueous NaCl and dried with Na_2SO_4. Evaporation of the Et_2O under vacuum gave VII as a moisture and O_2 sensitive, orange-yellow crystalline solid in ~95% isolated yield. IR (Nujol): ν_{CN} 2242 cm^{-1}. ^1H NMR (C_6D_6): δ 3.13 (s, 1 H), 2.67 (s, 2 H), 1.55 (s, 6 H), 1.53 (s, 6 H), 1.51 (s, 6 H), 1.44 (s, 6 H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 117.8, 80.3, 80.1, 80.0, 78.7, 73.4, 71.8, 14.5, 11.3, 9.67, 9.53, 9.34.

2-(Octamethylferrocenyl)ethaneisonitrile (VIII). A 200-mL round-bottom flask was equipped with a condenser, addition funnel, Ar inlet, and magnetic stirring bar. $LiAlH_4$ (1 g) and Et_2O (60 mL) were added to the flask and the mixture refluxed under Ar for 10 min. After cooling to room temperature, a solution of VII (1 g, 3.1 mmol) in 30 mL of anhydrous Et_2O was added slowly to the flask through the addition funnel. The mixture was then refluxed for 1 h and cooled to 0 °C. The excess $LiAlH_4$ was quenched with H_2O and the Et_2O layer was separated, washed with 5% NaOH solution and saturated aqueous NaCl, and dried with Na_2SO_4. Evaporation of solvent resulted in a brownish-yellow oil of 2-(octamethylferrocenyl)ethylamine in ~90% yield (0.9 g), which was used without further purification. ^1H NMR ($CDCl_3$): δ 3.22 (s, 1 H), 2.62 (t, 2 H), 2.32 (t, 2 H), 1.71 (s, 6 H), 1.69 (s, 6 H), 1.67 (s, 6 H), 1.62 (s, 6 H). 2-(Octamethylferrocenyl)ethylamine (0.4 g, 1.2 mmol) and 0.09 g of [*n*-Et_4N]Cl (phase-transfer catalyst) were dissolved in 15 mL of CH_2Cl_2 and 2 mL $CHCl_3$. A 10-mL aliquot of 50% NaOH solution was added to the mixture and the resultant mixture was stirred at room temperature for 30 min. After a CH_2Cl_2/H_2O workup procedure, the crude product was chromatographed on activated Al_2O_3 (3 cm × 12 cm), using Et_2O/hexanes (1:2) as eluent. The first orange-yellow band elution consists of unreacted 2-(octamethylferrocenyl)ethylamine; the second orange-yellow band was collected and upon removal of the solvent gave VIII as orange-yellow crystallization prisms in 40% isolated yield, mp 79 °C. IR (CH_2Cl_2): ν_{NC} 2151 cm^{-1}. ^1H NMR (C_6D_6): δ 3.07 (s, 1 H), 2.66 (t, 2 H), 2.26 (t, 2 H), 1.60 (s, 12 H), 1.57 (s, 6 H), 1.52 (s, 6 H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 82.8, 80.1, 79.9, 79.8, 78.8, 71.2, 41.4, 26.9, 11.4, 10.0, 9.9, 9.5. Anal. Calcd (Found): C, 71.80 (71.51); H, 8.32 (8.27); N, 3.99 (3.79).

(1-Mercapto-3,6-dithiaheptanyl)octamethylferrocene (IX) and Bis[2-(octamethylferrocenylmethylthio)ethyl] Sulfide (X). To a solution of

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[16] Kohl, F. X.; Jutzi, P. *J. Organomet. Chem.* **1983**, *243*, 119.

[17] Schimitt, V. G.; Ozman, S. *Chem. Ztg.* **1976**, *100*, 143.

[18] Olah, G. A.; Keumi, T. *Synthesis* **1979**, 112.

2-mercaptoethyl sulfide (1 g, 6.4 mmol, Aldrich) in THF (50 mL) was added dropwise 0.85 mL of *n*-BuLi (2.3 M in hexanes, 2 mmol) under Ar. A cloudy white solution was formed immediately. A solution of I [freshly prepared from 0.66 g of III (2 mmol) as described above] in acetone (50 mL) was added slowly with vigorous stirring. After stirring at room temperature for 5 min, the solvent was removed under vacuum to leave a yellow oily material. This was chromatographed on an activated Al_2O_3 column (3 cm × 12 cm). Elution with Et_2O/hexanes (1:1) yielded two orange-yellow bands. IX was isolated from the second band as an orange-yellow oil (0.7 g, 75% isolated yield). ^1H NMR (C_6D_6): δ 3.47 (s, 2 H), 3.12 (s, 1 H), 2.15–2.55 (m, 8 H), 1.80 (s, 6 H), 1.64 (s, 12 H), 1.56 (s, 6 H), 1.38 (t, 1 H). ^{13}C NMR (C_6D_6): δ 80.3, 80.2, 80.0, 79.4, 79.0, 71.2, 36.4, 32.6, 32.1, 29.3, 25.0, 11.5, 10.4, 10.0, 9.6. Anal. Calcd (Found): C, 59.46 (58.86); H, 7.18 (7.64); S, 21.70 (21.90). X was isolated from the first band as a yellow, crystalline solid (0.05 g, 7% isolated yield), mp 98 °C. ^1H NMR (C_6D_6): δ 3.48 (s, 4 H), 3.13 (s, 2 H), 2.53 (s, 8 H), 1.80 (s, 12 H), 1.65 (s, 12 H), 1.64 (S, 12 H), 1.55 (s, 12 H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 80.1, 79.8, 79.2, 78.8, 72.3, 71.0, 32.6, 31.8, 28.9, 11.1, 9.9, 9.5, 9.1. Anal. Calcd (Found): C, 65.11 (64.97); H, 8.07 (8.09); S, 12.42 (12.65). The ratio of IX to X in this synthesis depends on the ratio of the Li[RS^-] to I and the rate of addition of I. The yield of X can be improved dramatically by adding the Li[RS^-] reagent slowly to a solution containing excess I.

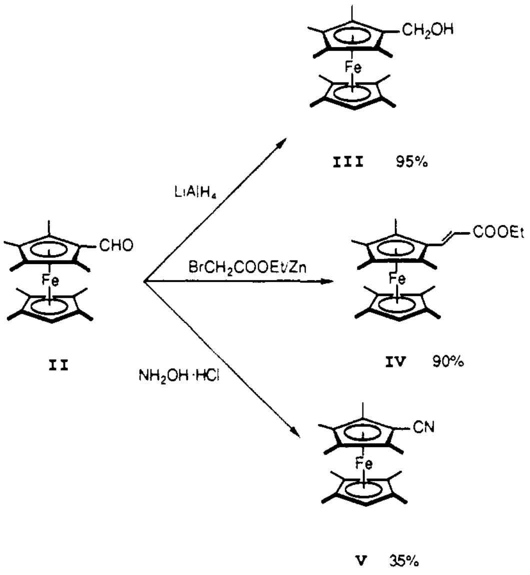
***N*-(Octamethylferrocenyl)aniline (XI).** To a solution of aniline (1 g) in THF (50 mL) was added a powder of I (freshly prepared from 0.33 g of III, 1 mmol) at room temperature under Ar. The solution was stirred for 5 min. The solvent was removed by using a rotary evaporator. The oily residue was chromatographed on activated Al_2O_3, and a yellow band was eluted with Et_2O. This was collected and the solvent and a small amount of aniline were removed under reduced pressure to give a yellow crystalline solid (85% yield), mp 84 °C. ^1H NMR ($CDCl_3$): δ 7.22 (m, 2 H), 6.62–6.73 (m, 3 H), 3.87 (s, 2 H), 3.40 (s, br, 1 H), 3.33 (s, 1 H), 1.79 (s, 6 H), 1.77 (s, 6 H), 1.76 (s, 6 H), 1.70 (s, 6 H). ^{13}C NMR ($CDCl_3$): δ 148.8, 129.4, 117.1, 112.5, 80.6, 79.9, 79.3, 70.2, 40.1, 11.0, 9.4, 9.3, 9.1. Anal. Calcd (Found): C, 74.44 (74.77), H, 8.25 (8.38), N, 3.47 (3.47).

***N*,*N*-Bis(octamethylferrocenyl)-1,4-phenylenediamine (XII).** To a solution of 1,4-phenylenediamine (0.43 g, 3.6 mmol) in THF (50 mL) was added 0.4 mL of 2.3 M *n*-BuLi. A solution of I (prepared from 1 mmol of III) in acetone (30 mL) was added. After 5 min the solution was concentrated to ~2 mL and chromatographed on an activated Al_2O_3 column (3 × 10 cm). Elution with C_6H_6 gave an orange band from which XII was isolated as an orange powder. Recrystallization from CH_2Cl_2/hexanes gave analytcally pure product (55%), mp 225 °C. ^1H NMR ($CDCl_3$): δ 6.59 (s, 4 H), 3.84 (s, 4 H), 3.30 (s, 2 H), 2.98 (s, 2 H), 1.78 (s, 12 H), 1.75 (s, 12 H), 1.74 (s, 12 H), 1.68 (s, 12 H). ^{13}C NMR ($CDCl_3$): δ 141.5, 114.5, 80.2, 80.1, 79.7, 79.5, 70.6, 41.6, 11.1, 9.5, 9.4, 9.2. Anal. Calcd (Found): C, 72.56 (72.56); H, 8.25 (8.35); N, 3.85 (3.93).

Functionalization of Surfaces. To immobilize nucleophiles onto a Pt or indium tin oxide (ITO) electrode surface, the ~1-cm^2 electrode was first sonicated in hexanes, CH_2Cl_2, and acetone each for 15 min, followed by an oxygen plasma etch at 100 mW for 5–20 min. In some cases electrodes pretreated in this manner were reacted directly with I by immersion in an acetone solution of ~1 mM I for a few minutes. More typically, the pretreated electrodes were heated in neat $(MeO)_3Si(CH_2)_3X$ (X = NH_2, SH) at 60–70 °C for 24 h to attach the NH_2 or SH reagents. After sonication in CH_2Cl_2 and acetone to remove unbound reagent, the electrodes were then immersed in an acetone solution of ~1 mM I for a few minutes. The electrodes were then washed thoroughly with acetone and Et_2O and dried. The electrochemical response of the electrodes was recorded in CH_3CN/0.1 M [n-Bu_4N]PF_6 containing no added electroactive species.

SiO_2 powder (Alfa; 400 m^2/g) was used in some experiments to study reactions of I with surface-bound nucleophiles. The SiO_2 was first heated to 150 °C at 0.01 Torr for >10 h to drive off excess H_2O. The powder was then reacted directly with I at room temperature by adding the powder to an acetone solution of ~1–10 mM I. The nearly white powder was isolated by filtration, washed with acetone, and dried. Oxidation in air yields a pale blue powder. Analysis of the powder shows 0.14% Fe by mass, consistent with a coverage of octamethylferrocenyl units of 6.3 × 10^{-12} mol/cm^2. In other experiments the pretreated SiO_2 was reacted first with 0.1 M $(MeO)_3Si(CH_2)_3NH_2$ in toluene at reflux for 4 h. The resulting [SiO_2]–$Si(CH_2)_3NH_2$ was filtered and washed with a large quantity of toluene and Et_2O, and dried under vacuum. Analysis shows 6.98% C and 2.58% N by mass consistent with 4.6 × 10^{-10} mol/cm^2 of NH_2 units. The slight excess C from analysis may signal incomplete hydrolysis of the $Si(OMe)_3$ group of the $(MeO)_3Si(CH_2)_3NH_2$. The amine functionalized powder was then reacted with I by adding the powder to an acetone solution of ~1 mM I and stirring for a few minutes. The yellow powder was isolated by filtration, washed with acetone and Et_2O, and dried under vacuum. Analysis (Fe and N) is consistent with reaction of 12% of the NH_2 units with the carbocation.

Scheme I. Some Reactions of Octamethylformylferrocene (II)



Results

(a) Synthesis of the Precursor Leading to I, Octamethylformylferrocene (II) and Its Reactions. We have found that a precursor to I, octamethylformylferrocene (II), can be prepared readily in 95% isolated yield by formylation of octamethylferrocene with *N*,*N*′-dimethylformamide/$OPCl_3$ (*Vilsmeier* reaction).[11] The formylation of octamethylferrocene proceeds in a higher yield than that of ferrocene (~80% yield),[19] which can be attributed to the higher electron density of octamethylferrocene compared with that of ferrocene. Reduction of II with $LiAlH_4$ in Et_2O gives essentially quantitative yields (~95% isolated) of (octamethylferrocenyl)methanol (III). In preparing the alcohol III by reduction of II with $LiAlH_4$, however, care must be taken in not adding excess $LiAlH_4$ which results in decomposition of III.

In addition to facile conversion to III by reduction, II can also be converted to other octamethylferrocene derivatives in a straightforward manner, Scheme I. The condensation of II and $BrCH_2COOEt$ (*Reformatsky* reaction)[10] followed by H_2O elimination in the presence of I_2 gives the octamethylferrocenyl-α,β-unsaturated ester IV. ^1H NMR reveals only two olefinic resonances with J = 16.1 Hz, consistent with formation of only the trans isomer. II is conveniently converted to octamethylcyanoferrocene (V) in one step by reaction with $NH_2OH \cdot HCl$ in formic acid.[18]

(b) Synthesis of (Octamethylferrocenyl)methyl Carbocation I and Its Reactions with Nucleophiles. Addition of a solution of $HBF_4 \cdot Et_2O$ at room temperature to a Et_2O solution of III results in the instantaneous precipitation of I as an orange-red, solid. I, as isolated, is fairly stable at room temperature in the absence of moisture and is easily handled for periods of the order of 30 min. The UV–vis spectrum of I in CH_2Cl_2 solution, Figure 1, shows a well-defined peak in the visible region (~480 nm) with an extinction coefficient of ~170, close in position and intensity to the ligand field adsorption of octamethylferrocene. The ^1H and ^{13}C NMR resonances of I are sharp, consistent with formulation of I as a diamagnetic Fe(II) species. ^1H NMR shows that all proton resonances of I shift downfield compared with those of neutral octamethylferrocene derivatives. A two-proton resonance at 5.27 ppm corresponding to the methylene protons bearing the positive charge is especially shifted. The ^{13}C NMR spectrum is as expected, based on the formulation of I as in eq 1. The ^{13}C

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(19) (a) Broadhead, G. D.; Osgerby, J. M.; Pauson, P. L. *J. Chem. Soc.* **1958**, 650. (b) Rosenblum, M.; Banerjee, A. K.; Danieli, N.; Fish, R. W.; Schlatter, V. *J. Am. Chem. Soc.* **1963**, *85*, 316.

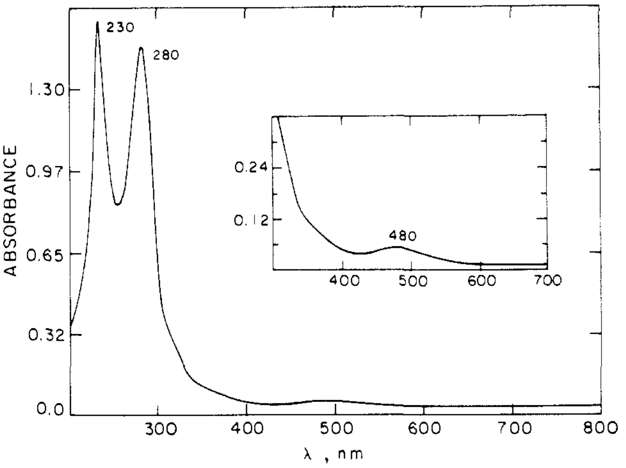
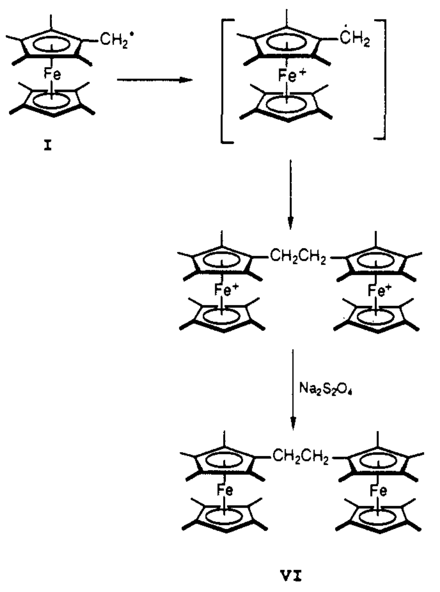


Figure 1. UV-vis spectrum of 1.5×10^{-5} M solution of I in CH_2Cl_2. The cell path length is 1.00 cm. The inset shows the visible absorbance of a 1.5×10^{-3} M solution of I in CH_2Cl_2 with a cell path length of 0.2 cm.

Scheme II. Dimerization of I

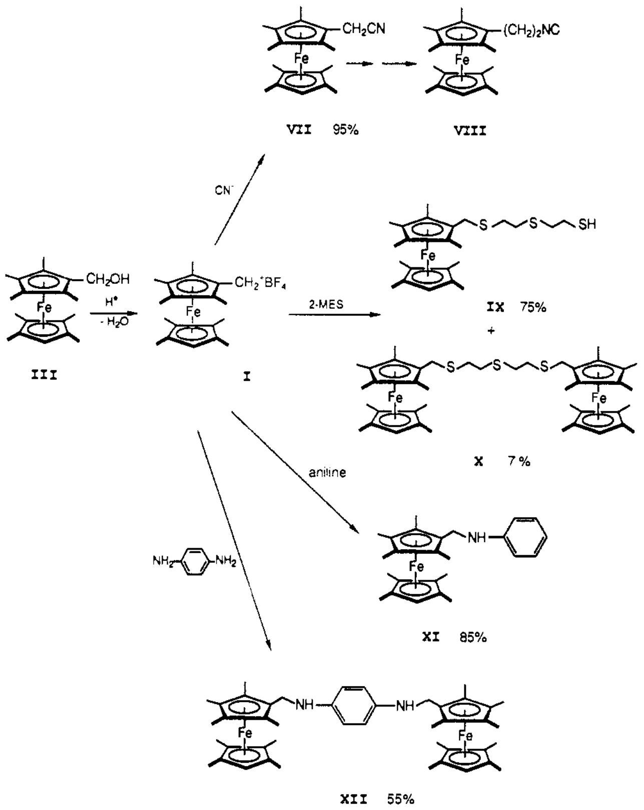


resonances for the carbon bearing the positive charge, C_{exo}, and the adjacent carbon, C_α, are as downfield as 107 ppm, ~15 ppm further downfield than other cyclopentadienyl ring carbons.

At room temperature in the solid state or in solution, I gradually dimerizes (under inert atmosphere) to a green paramagnetic species. This material is 1,2-bis(octamethylferroceniumyl)ethane, formed via intramolecular electron transfer and subsequent dimerization of the C-centered radical, Fe(III) cationic species, Scheme II. Such a mechanism is consistent with the reported transformations of other ferrocenylmethyl carbocations.[20] Reduction of 1,2-bis(octamethylferriceniumyl)ethane with either cobaltocene in CH_2Cl_2 or $Na_2S_2O_4$ in aqueous solution results in the formation of 1,2-bis(octamethylferrocenyl)ethane (VI). Solutions of I are more durable than pure I. The dark-red solution of ~1 mM I in acetone is stable for up to 24 h under an inert atmosphere at room temperature and much longer at low temperatures. The slower reaction presumably results from the dilution and from the stabilization of the C-centered cation by the coordination of the oxygen lone-pair electrons of acetone.

A large variety of ferrocenyl carbocations have been isolated previously.[2] However, they are generally stable only at temperatures <−20 °C for short periods of time and have been isolated only when stabilized by one or more substituents on the methyl carbon. The carbocation derived from III is more stable due to the electron-rich nature of the octamethylferrocenyl group, which stabilizes the carbocation.

Scheme III. Some Reactions of I with Nucleophiles



We have carried out reactions of I with a variety of nucleophiles to synthesize a series of octamethylferrocene derivatives, Scheme III. All reactions proceed rapidly at room temperature and are essentially complete upon mixing the starting materials. I reacts with CN^- to produce (octamethylferrocenyl)methanenitrile (VII), which may be converted to the 2-(octamethylferrocenyl)ethaneisonitrile (VIII) by standard procedures.[21] The yield of VII is essentially quantitative.

Reactions of I with SH and NH_2 groups have also been explored. For example, reaction of I and 2-mercaptoethyl sulfide results in formation of octamethylferrocenyl sulfides (IX and X). Reaction of the RSH reagent directly gives lower yields of the produce compared to reaction with the anionic RS^- as the Li^+ salt. The reactivity of I with nitrogen donor, NH_2, nucleophiles has been examined by exploring the reaction with aniline or 1,4-phenylenediamine. Both reactions proceed readily to give high yields of *N*-(octamethylferrocenyl)aniline and *N*,*N'*-bis(octamethylferrocenyl)-1,4-phenylenediamine, respectively. Interestingly, we did not isolate any *N*-(octamethylferrocenyl)-1,4-phenylenediamine when a 5:1 ratio of 1,4-phenylenediamine to I was used and a solution of I was added dropwise to the 1,4-phenylenediamine solution. The uptake of the second (octamethylferrocenyl)methyl carbocation is presumably very fast owing to the greater electron density on the second N center upon adding the first octamethylferrocenyl group.

(c) Reactions of (Octamethylferrocenyl)methyl Carbocation I with Surface-Immobilized Nucleophiles. The facile reaction of I with various nucleophiles provides an interesting method of surface modification with octamethylferrocene derivatives. In principle, the (octamethylferrocenyl)methyl carbocation should be able to react with surfaces by reaction with surface-anchored nucleophiles, in a manner represented by eq 2. We have studied the reactions of I with nucleophiles such as RNH_2 and RSH which have been immobilized on surfaces of Pt or indium tin oxide

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(20) (a) Fedin, P. V.; Kreindlin, A. Z.; Fadeeva, S. S.; Rybinskaya, M. I. *J. Organomet. Chem.* **1985**, *292*, 257. (b) Cais, M.; Ashkenazi, P.; Dani, S.; Gottlieb, J. *J. Organomet. Chem.* **1977**, *124*, 49. (c) Renehart, C. J., Jr.; Michejda, C. J.; Kittle, P. A. *J. Am. Chem. Soc.* **1959**, *81*, 3162.

(21) *Isonitrile Chemistry*; Ugi, I., Ed.; Academic Press: New York, 1971.

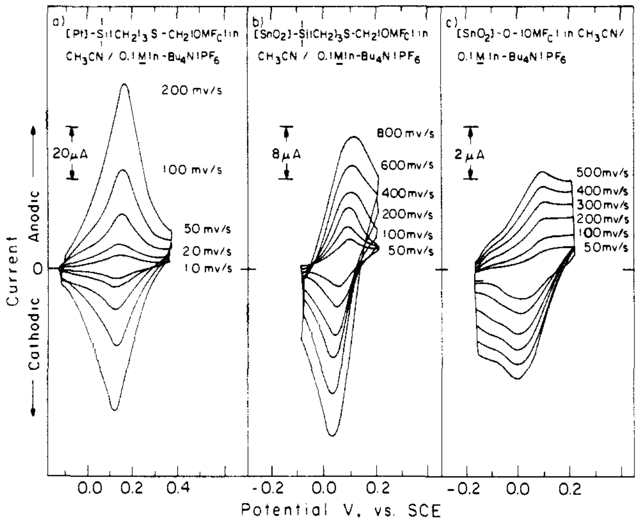
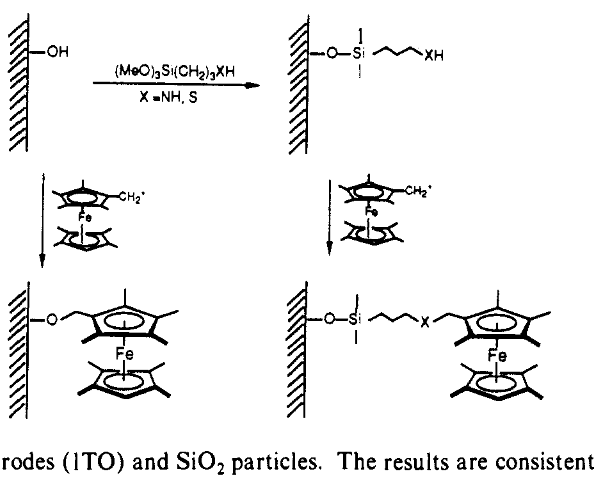


Figure 2. (a) Scan rate dependence of cyclic voltammogram for a derivatized Pt electrode derived from reaction of 1 with a Pt electrode that had been pretreated with $(MeO)_3Si(CH_2)_3SH$. The electrode area was ~1 cm^2. (b) Scan rate dependence of cyclic voltammogram for a derivatized ITO electrode derived from reaction of 1 with an ITO electrode that had been pretreatd with $(MeO)_3Si(CH_2)_3SH$. The electrode area was ~0.5 cm^2. (c) Scan rate dependence of cyclic voltammograms for an ITO electrode after reaction with 1.

Scheme IV. Modification of Surfaces with 1



electrodes (ITO) and SiO_2 particles. The results are consistent with the covalent bonding of the octamethylferrocenyl unit to the surfaces, Scheme IV.

Figure 2 includes the scan rate dependence of the cyclic voltammogram of a modified Pt electrode derived from reaction of 1 with a Pt electrode pretreated with $(MeO)_3Si(CH_2)_3SH$. The presence of a persistent cyclic voltammogram with a peak near +0.1 V vs SCE confirms the attachment of the octamethylferrocenyl unit. Integration of the anodic peak gives a surface coverage of ~5 × 10^{-10} mol/cm^2, or about one monolayer. Figure 2 also shows the scan rate dependence of the cyclic voltammogram associated with an ITO electrode that has been pretreated with $(MeO)_3Si(CH_2)_2SH$, followed by reaction with I. Similar results are found for Pt or ITO electrodes first pretreated with $(MeO)_3Si(CH_2)_3NH_2$ followed by reaction with I. Treatment of a Pt electrode, which has not been derivatized with $(MeO)_3Si(CH_2)_3X$ (X = SH or NH_2), with an acetone solution of 1 results in no attachment of the octamethylferrocenyl unit, as measured by electrochemistry. However, treatment of an ITO electrode with an acetone solution of I results in attachment of a small amount of I (Figure 2), presumably via reaction of I with surface OH groups. The coverage is usually in the range of 1 × 10^{-11}–3 × 10^{-11} mol/cm^2, or less than 10% of a monolayer.

We have applied CP/MAS solid-state NMR to characterize 1 confined on SiO_2 particle surfaces via reaction with pendant $(CH_2)_3NH_2$ groups. Figure 3 (top) shows the ^{13}C CP/MAS NMR spectrum of SiO_2 powder derivatized only with $(MeO)_3Si(CH_2)_3NH_2$, $[SiO_2]$-$Si(CH_2)_3NH_2$. Elemental analysis of the derivatized powder shows 4.6 × 10^{-10} mol/cm^2 of NH_2 units, assuming uniform coverage of the solid with a surface area of 400 m^2/g. As expected, three peaks due to the carbons of the propyl group were observed, the peak at ~11 ppm for the carbon adjacent to the Si, the peak at 27 ppm for the number two carbon, and the peak at ~45 ppm for the carbon adjacent to the NH_2 group. The shoulder at 50 ppm is due to the methoxy group resulting from incomplete hydrolysis of the starting $(MeO)_3Si(CH_2)_3NH_2$. These ^{13}C resonances are assigned by comparing the position of the resonances with those measured for $(MeO)_3Si(CH_2)_3NH_2$ in solution. After reaction of $[SiO_2]$-$Si(CH_2)_3NH_2$ with I, the ^{13}C NMR spectrum of a sample shows new resonances associated with the surface-confined octamethylferrocenyl unit, Figure 3 (bottom). Analysis shows ~12% of the N's has been functionalized with the carbocation. In addition to the peaks due to the propyl carbons in the ^{13}C NMR, there is a new, intense peak at ~10 ppm attributable to methyl carbons on the cyclopentadienyl rings of octamethylferrocenyl units, a peak at ~80 ppm due to cyclopentadienyl ring carbons having a methyl substituent, and a peak at ~72 ppm due to the cyclopentadienyl ring carbon without a methyl substituent. Thus, solid-state NMR unequivocally establishes the intact attachment of octamethylferrocenyl units to the SiO_2 surface via the route illustrated in Scheme IV. Importantly, no significant ^{13}C resonances are observed other than those expected.

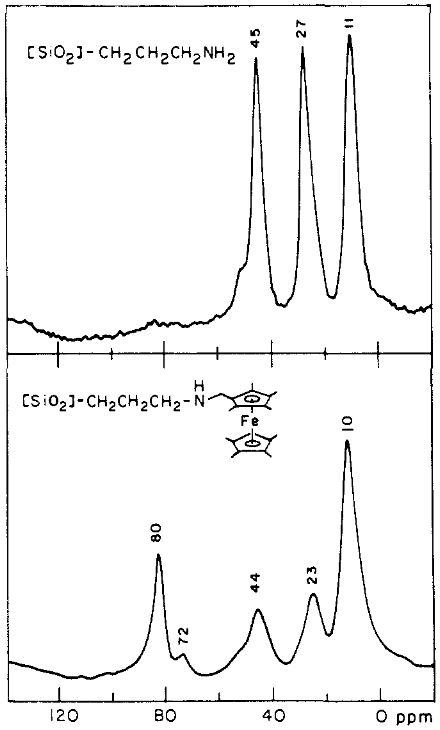


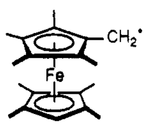
Figure 3. Top: ^{13}C CP/MAS solid-state NMR spectrum of $[SiO_2]$–$(CH_2)_3NH_2$ from reaction of high surface area SiO_2 and $(MeO)_3Si(CH_2)_3NH_2$. The peak at ~45 ppm is due to the carbon next to nitrogen, the peak at ~27 ppm is due to the number two carbon, and the peak at ~11 ppm is due to the carbon adjacent to silicon. Bottom: ^{13}C CP/MAS solid-state NMR spectrum of $[SiO_2]$–$(CH_2)_3NH$–(octamethylferrocenyl)methyl. In addition to the peaks due to propyl carbons, the peak at ~80 ppm is due to the cyclopentadienyl carbons with methyl substituents, the peak at ~72 ppm is due to the cyclopentadienyl carbon without a methyl substituent, and the intense peak at ~10 ppm overlapping the resonances for the carbon adjacent to silicon is due to methyl carbons.

Reaction of SiO_2 powder directly with 1 in an acetone solution at room temperature results in a powder with no apparent color changes compared with the starting SiO_2 powder. However, exposure of this product to air for a few hours results in color change to a pale-blue powder, indicating oxidation of surface-confined octamethylferrocenyl units to octamethylferrocenium units by O_2. These results are consistent with attachment of octamethylferrocenyl units to the SiO_2 surface directly via reaction of I with surface OH groups. Analysis of the powder indicates only 6.3 × 10^{-12} mol/cm^2 of I is attached to the surface, far less than when I reacts with SiO_2 powder that has been first pretreated with $(MeO)_3Si(CH_2)_3NH_2$.

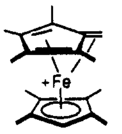
Discussion

The results described above illustrate some examples of synthesis of octamethylferrocene derivatives via the reaction of I with various nucleophiles. The resulting neutral products can generally be separated easily from the starting ionic species by column chromatography. The reaction between I and anionic RS^- usually gives higher isolated yields than those from the reaction between I and the analogous RSH. Reaction of I with CN^- proceeds essentially quantitatively. Thus, good, anionic nucleophiles react with I to give product in excellent yield. The advantage of our synthetic method is that a large number of octamethylferrocene derivatives can be made simply by varying the nucleophiles used. Preliminary results[22] show that I reacts with pyridine derivatives to give the expected pyridinium products in excellent yield. RO^- is also found to react to give good yields of the expected ethers. Not surprisingly, exposure of I to H_2O regenerates the alcohol III. Our method is especially convenient for preparation of a series of octamethylferrocene derivatives with similar redox properties having variable functional groups and side-chain lengths. Studies of Au and Pt electrode surfaces functionalized with VIII or IX are in progress, in order to investigate the attachment chemistry via SH or NC groups.[23]

There has been much speculation about the structure of ferrocenylmethyl carbocation derivatives.[2] From the chemistry found for I it is evident that there is substantial cationic character on the methyl carbon of the (octamethylferrocenyl)methyl carbocation. Thus, the electronic structure of I can be formulated as A. Interestingly, according to the 18e$^-$ rule structure B, an Fe-centered cation with a tetramethylfulvene ligand, can be considered. The crystal structure of ferrocenyldiphenylcyclopropenium cation has been determined previously,[24] and the result shows that although the Fe–C_{exo} distance (2.85 Å) in ferrocenyldiphenylcyclopropenium is not indicative of a significant bonding interaction, the displacement of the C_α–C_{exo} bond from the adjacent cyclopentadienyl plane toward Fe (14.6°) cannot be ignored. The ^{13}C NMR spectrum of I shows that resonances for C_{exo} and C_α carbons, 107 and 106 ppm, respectively, are far downfield from those for other cyclopentadienyl ring carbons, which have resonances in the range of 89–94 ppm. This is consistent with the formulation of I as A, a carbon-centered cation, and with the reaction chemistry described. The optical absorption spectrum of I can also be regarded as consistent with the formulation shown in A: the lowest absorption (~480 nm, $\epsilon \approx$ 170 M^{-1} cm^{-1}) is somewhat red-shifted from that of octamethylferrocene (~430 nm, $\epsilon \approx$ 130 M^{-1} cm^{-1})[7a] itself, but would appear to be a ligand field absorption like that for ferrocene.[1d] However, the optical properties of a species like B are not known and could also have a ligand field first absorption. Obviously, an X-ray crystal structure of I would be highly desirable and efforts are underway to prepare suitable crystals. For now, it seems that structure A is the best view for I, because we obtain high yields of the expected product, up to 95%, upon reaction with CN^-. If B were the correct formulation, it would seem that attack would occur at the methyl-substituted carbon, especially for a small nucleophile like CN^-.

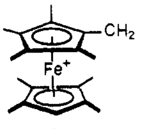


A



B

The dimerization of I (Scheme II) suggests a role for the diradical C, featuring a C-centered radical and an Fe(III) center.



C

Such species have been suggested previously in the chemistry of other ferrocenylmethyl carbocations, but it is likely that such a formulation for I represents a more energetic structure than A. The fact that the ^1H and ^{13}C NMR of I show sharp resonances is consistent with I being a diamagnetic species as in A. Thus, the diradical cation C is only a transient in the dimerization to form a C–C coupled product.

The reactions of I with surface-confined nucleophiles results in attachment of octamethylferrocenyl units to surfaces. The low attachment yield of octamethylferrocenyl units to surfaces via reaction of I directly with ITO electrodes or with SiO_2 powder may be due to the weak nucleophilicity of surface OH groups, or due to steric constraints. However, by introducing nucleophiles to the surfaces first, followed by reaction with I, up to about one monolayer of octamethylferrocenyl units can be immobilized onto the surfaces. Analysis of the SiO_2 powders derivativzed first with $(MeO)_3Si(CH_2)_3NH_2$ and then with I shows relatively modest yields of the expected attached ferrocene. Presumably, deprotonation reagents such as 2,6-dimethylpiperidine or triisopropylamine will be useful in improving the yield. The electrode (Pt or ITO) surfaces have not yet been analyzed for yield, but the electrochemical coverage from reaction of I with the SH or NH_2 groups is about one monolayer in both cases. The preliminary results demonstrated for surfaces suggest significant opportunities for detailed studies of tailored surfaces from direct reaction with I or from using the new derivatizing reagents prepared from I, such as the isonitrile VIII or the thiol IX.

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Registry No. I, 128925-11-1; II, 128925-12-2; III, 128925-13-3; IV, 128925-14-4; V, 128925-15-5; VI, 128925-16-6; VII, 128925-17-7; VIII, 128925-18-8; IX, 128925-19-9; X, 128971-32-4; XI, 128925-20-2; XII, 128925-21-3; $BrCH_2COOEt$, 105-36-2; 2,3,4,5-tetramethyl-2-cyclopentenone, 54458-61-6; octamethylferrocene, 59568-28-4; cobaltocene, 1277-43-6; 2-mercaptoethyl sulfide, 3570-55-6; (octamethylferrocenyl)ethylamine, 128925-22-4; aniline, 62-53-3; 1,4-phenylenediamine, 106-50-3.

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