

## Permercuration of substituted ferrocenes: assessment of the degree of mercuration

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### Abstract

Mono- and disubstituted ferrocenes react with excess mercuric acetate (at least eight or nine equivalents) to afford highly insoluble mixtures of polymercurated ferrocenes. In the case of 1,1'-dimethylferrocene, the mercuration product is composed of minor amounts of the octamercurated and hexamercurated ferrocenes, with the heptamercurated ferrocene being the major product. This analysis is based upon results of chlorination and bromination studies of the mercuration species. It is proposed that exhaustive mercuration fails due to the extreme insolubility of the higher mercuration products.

*Keywords:* Iron; Ferrocene; Mercury; Metallocenes; Cyclopentadienyl; Mercuration

### 1. Introduction

Mercuration is one of the fundamental reaction processes that aromatic organic compounds undergo [1,2]. While monomercuration of benzenoid compounds is the most prevalent reaction mode, polymercurated and even complete replacement of the aromatic hydrogens has been observed in certain systems. For example, benzene, anisole, furan, thiophene, and other aromatics can be permercuration upon treatment with mercuric salts at elevated temperatures [3]. Less is known about the mercuration of organometallic compounds bearing aromatic ligands [4,5]. Most of the mercuration studies have used ferrocene [4], which undergoes mono- and dimercurated upon treatment with mercuric acetate. Several other brief reports have described the mono- and dimercurated of ruthenocene [5a], the mono- and dimercurated of cyclopentadienylmanganese tricarbonyl [5b], and the tetramercurated of cyclobutadiene iron tricarbonyl [5c]. Ferrocene itself has been claimed to undergo decamercurated upon treatment with mercuric trifluoroacetate in ethanol:diethyl ether at ambient temperature [6a]. Additionally, 1,1'-dimethylferrocene

was reported to be octamercurated under similar conditions [6b]. Cyclopentadienylmanganese tricarbonyl is pentamercurated upon treatment with mercuric trifluoroacetate [6c].

We have recently reported that the cyclopentadienyl ligands in ruthenocene [7a,b], pentamethylruthenocene [7c], osmocene [7d], cyclopentadienylmanganese tricarbonyl [7e,8], and cyclopentadienylrhenium tricarbonyl [7e] can be permercuration upon treatment with mercuric acetate under mild conditions. The degree of mercuration was established by a combination of NMR, microanalysis, and halogenation studies. We also examined the decamercurated of ferrocene, but found that a mixture of decachloroferrocene, nonachloroferrocene, and octachloroferrocene was obtained upon chlorination of the mercuration product, suggesting that ferrocene was not fully decamercurated [7b]. Unfortunately, the low solubility and lack of groups with convenient NMR properties did not allow us to quantify the chlorinated ferrocene mixture. We sought to extend the mercuration to substituted ferrocenes, which might allow precise analyses of the product(s) derived from halogenation. Herein we report the mercuration of 1,1'-dimethylferrocene, 1,1'-diacetylferrocene, acetylferrocene, 1,1'-ferrocene dicarboxylic acid, ferrocene carboxylic acid, and ferrocene carboxaldehyde. Halogenation studies re-

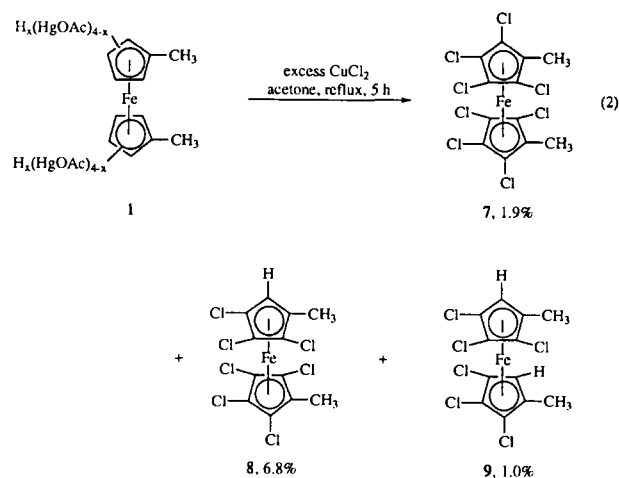
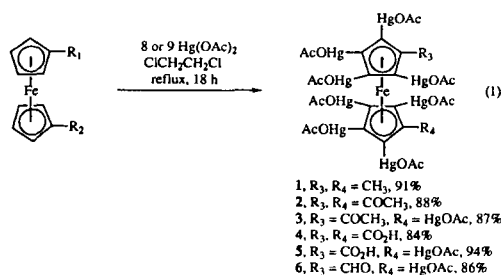
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veal that the substituted ferrocenes do not undergo exhaustive permercuration and are therefore not useful intermediates for the synthesis of new persubstituted ferrocenes.

## 2. Results

Treatment of the six mono- and disubstituted ferrocenes with nine and eight equivalents of mercuric acetate respectively in refluxing 1,2-dichloroethane for 18 h afforded the mercurated ferrocenes 1–6 as yellow to orange insoluble powders that precipitated from the reaction media (Eq. 1). Yields ranged between 84 and 94%, assuming a permercurated formulation. Complexes 1–6 were insoluble in all common organic solvents, which precluded analysis by solution NMR methods. The ferrocenes were characterized by melting points, microanalyses, and IR spectroscopy. None of the materials melted, but rather exhibited broad decomposition ranges between 180 and 250 °C, with concurrent evolution of liquid mercury. The infrared spectra were dominated by absorptions characteristic of the mercury–acetate linkages between 1579 and 1555 (vs) and 1406 and 1360 (s)  $\text{cm}^{-1}$ . The ketone group in 3 showed a weak absorption at 1691  $\text{cm}^{-1}$ , while the aldehyde functionality in 6 exhibited a weak absorption at 1700  $\text{cm}^{-1}$ . The carbonyl stretch in 2 was obscured by the strong acetate absorption. Medium intensity, broad absorptions from the carboxylic acid functionality were observed for 4 (3405  $\text{cm}^{-1}$ ) and 5 (3320  $\text{cm}^{-1}$ ), indicating that decarboxylation did not occur during the mercuration process. The carbon and hydrogen microanalyses hovered around the values calculated for the permercurated compounds, but could not be obtained within  $\pm 0.4\%$ . In addition, the calculated carbon and hydrogen contents of an octamercurated structure were within ca. 1.6% of a hexamercurated formulation (e.g., Anal. Calc. for  $\text{C}_{10}(\text{HgOAc})_8(\text{CH}_3)_2\text{Fe}$ : C, 14.73; H, 1.32. Anal. Calc. for  $\text{C}_{10}\text{H}_2(\text{HgOAc})_6(\text{CH}_3)_2\text{Fe}$ : C, 16.32; H, 1.48). Hence, the above data could not conclusively establish the degree of mercuration in 1–6.

Halogenation reactions were addressed as a method to probe the degree of mercuration in 1–6. However,



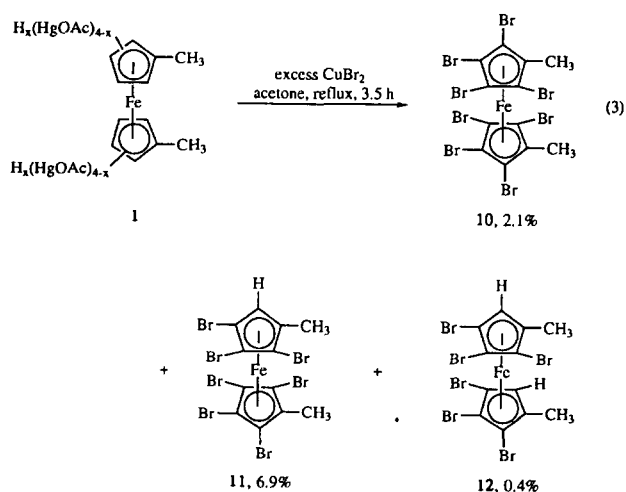
treatment of 1–6 with cupric chloride in acetone, cupric bromide in acetone, or potassium tribromide in water/methanol (conditions we have previously used to replace mercury by halogen [7]) afforded deep green solutions indicative of ferrocene oxidation. Only in the case of 1 was it possible to isolate any halogenated ferrocenes in pure form. In order to obtain enough product for careful characterization, the chlorination of 1 was conducted on a large scale (ca. 2.0 mmol) using cupric chloride (Eq. (2)). Chlorination under these conditions afforded an inseparable 20:70:10 mixture of 1,1',2,2',3,3',4,4'-octachloro-5,5'-dimethylferrocene (7, 1.9%), 1,1',2,2',3,3',4'-heptachloro-5,5'-dimethylferrocene (8, 6.8%), and 1,1',2,2',3,3'-hexachloro-5,5'-dimethylferrocene (9, 1.0%). In addition, four other unidentified chlorinated ferrocenes were observed, although they constituted no more than 5 mol.% of the chlorinated ferrocene mixture. The identity and distribution of 7–9 were established by a combination of GLC, GLC/MS, and  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR analyses. The principal identification was by GLC/MS. Ferrocenes 7–9 showed molecular ions under electron impact conditions, with observed isotope distributions for the molecular ion envelope that were identical to the calculated patterns.

Using the approximate ratios of compounds 7, 8, and 9 derived from GLC analysis, it was possible to assign the resonances in the  $^1\text{H}$  NMR. Complex 7 showed a singlet for the methyl groups at  $\delta$  1.92, complex 8 showed resonances at  $\delta$  4.09 (s,  $\text{C}_5\text{HCl}_3\text{CH}_3$ ), 1.96, and 1.90 (s,  $\text{C}_5\text{HCl}_3\text{CH}_3$  and  $\text{C}_5\text{Cl}_4\text{CH}_3$ ), while 9 showed resonances at  $\delta$  4.33 (s,  $\text{C}_5\text{HCl}_3\text{CH}_3$ ) and 1.97 (s,  $\text{C}_5\text{HCl}_3\text{CH}_3$ ). The 121 MHz  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of the mixture of 7–9 was recorded, but could only be partially assigned due to the large number of chlorinated carbon resonances. Methyl resonances were observed for 7 (7.72 ppm), 8 (9.36, 8.11 ppm), and 9

(8.32 ppm). The cyclopentadienyl carbons bearing hydrogens appeared at 71.51 ppm for **8** and 71.28 ppm for **9**. The cyclopentadienyl carbon bearing the methyl group resonated at 80.18 ppm for **7**, 82.77 and 79.23 ppm for **8**, and was not observed for **9**. The chlorinated carbons could be tentatively assigned to **7** (89.09, 89.04 ppm) and **8** (91.64, 91.25, 91.09, 90.00, 89.66, 89.60, 89.54 ppm), based upon peak intensities. The chlorinated carbon resonances for **9** were not of sufficient intensity to allow assignment. For comparison, 1,1'-dimethylferrocene showed resonances in the  $^1\text{H}$  NMR (chloroform-*d*, 23 °C) at  $\delta$  4.00 (s,  $\text{C}_5\text{H}_2\text{H}'_2\text{CH}_3$ ) and 2.00 (s,  $\text{C}_5\text{H}_2\text{H}'_2\text{CH}_3$ ) and in the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (chloroform-*d*, 23 °C) at 81.83 (s, C- $\text{CH}_3$ ), 69.77 (s, C-H), 67.79 (s, C-H), and 14.40 (s,  $\text{CH}_3$ ) ppm. Complexes **8** and **9** are depicted as single isomers, based upon the NMR data. We propose that the carbon adjacent to the methyl group would be the most sterically encumbered position where the last mercuriation is least likely to occur. Therefore, the hydrogens in **7** and **8** are depicted in this position.

In order to determine if **1** could be obtained as the pure octamercurated compound, the mercuriation of 1,1'-dimethylferrocene was repeated using 12 equivalents of mercuric acetate and a reflux time of 24 h. Workup afforded a mixture of hexa-, hepta-, and octamercurated ferrocenes in an approximate yield of 93%. Chlorination of this material using the conditions described above yielded a mixture of **7** (1.3% isolated yield), **8** (5.3% isolated yield), and five other minor ferrocene products ( $\leq 0.3\%$  yield). Thus, neither the yield of chlorinated ferrocenes nor the ratio of **7**:**8** was substantially affected by using excess mercuric acetate and a longer reflux.

The analogous bromination of **1** was conducted using cupric bromide in refluxing acetone (Eq. (3)). Workup afforded an inseparable 22:74:4 mixture of 1,1',2,2',3,3',4,4'-octabromo-5,5'-dimethylferrocene (**10**,



2.1% yield based upon **1**), 1,1',2,2',3,3',4-heptabromo-5,5'-dimethylferrocene (**11**, 6.9% yield based upon **1**), and 1,1',2,2',3,3'-hexabromo-5,5'-dimethylferrocene (**12**, 0.4% yield based upon **1**). Three other unidentified brominated ferrocenes were observed in the  $^1\text{H}$  NMR spectrum, although they constituted no more than 10 mol.% of the sample. Identification of **10**–**12** was based upon GLC, mass spectrometry, and correlation of the  $^1\text{H}$  NMR resonances with those of **7**–**9**. Ferrocenes **10**–**12** showed molecular ions under electron impact conditions, with observed isotope distributions for the molecular ion envelopes that were identical to the calculated patterns.

### 3. Discussion

There are two possible reasons for the observed mixture of halogenated ferrocenes obtained from **1**. The first is to assume that the halogenation product mixture is an accurate reflection of the mercurated ferrocene mixture. If this is the case, halogenation results suggest that **1** is a mixture of about 20% octakis(acetoxymercurio)dimethylferrocene, 70% heptakis(acetoxymercurio)dimethylferrocene, and 10% hexakis(acetoxymercurio)dimethylferrocene. We have previously reported that analogous halogenation reactions of decakis(acetoxymercurio)ruthenocene [7b] and decakis(acetoxymercurio)osmocene [7d] proceed without detectable incorporation of hydrogen into the products. Accordingly, it is a reasonable assumption that hydrodemercuration (i.e. replacement of  $\text{HgOAc}$  group by hydrogen) does not occur to a significant extent during halogenations of **1**. The calculated carbon and hydrogen contents for **1**, assuming it to be a mixture of hexa-, hepta-, and octamercurated ferrocenes that reflect the halogenation mixtures (Anal. Found: C, 15.72; H, 1.57. Calc.: C, 15.38; H, 1.38), are much closer to the experimentally observed values than those calculated for pure octakis(acetoxymercurio)dimethylferrocene. While this analysis is tenuously based solely upon a microanalysis, complexes **3**–**6** also show carbon and hydrogen microanalysis values that are slightly higher than the theoretical values for permercurated structures. Such values suggest that **3**–**6** are also mixtures of mercurated ferrocenes wherein the fully mercurated species is not the major product.

A second possibility is that the failure to obtain **7** as the major product from halogenation of **1** results from selective oxidation of the octamercurated compound, compared with the hepta- and hexamercurated analogs. We have recently reported that the metal center in pentakis(acetoxymercurio)cyclopentadienylmanganese tricarbonyl is slightly more electron rich than in cyclopentadienylmanganese tricarbonyl [7e], as deter-

mined by the position of the carbonyl absorptions in the infrared spectra. Thus, the octamercurated ferrocene should be the most easily oxidized, while the hexamercurated ferrocene should be the least easily oxidized. If this scenario is correct, then it is possible that the octamercurated product is actually the major constituent of **1**, but it is selectively oxidized under the halogenation conditions. However, the small carbonyl shifts observed in the mercurated manganese system, relative to cyclopentadienylmanganese tricarbonyl, suggest that the electronic donating ability of the acetoxymercurio group is correspondingly small. Thus, differences in oxidation potentials between octa-, hepta-, and hexamercurated dimethylferrocene are probably very small, which would not allow selective oxidation of the octamercurated complex. In addition, the microanalysis values discussed above do not support the idea of the octamercurated ferrocene being the major constituent of **1**.

The results described herein make us sceptical about previous reports claiming the decamercuration of ferrocene [**6a**] and octamercuration of 1,1'-dimethylferrocene [**6b**]. We have previously described the polymercuration of ferrocene using mercuric trifluoroacetate in ethanol:diethyl ether (conditions claimed to give decamercurated ferrocene [**6a**]) [**7b**]. It is interesting to compare the attempted permercurations of **1–6**, which do not give single permercurated products, with those of ruthenocene and osmocene, which afford only the decamercurated metallocenes. While it is clear that some of the octamercurated product is present in **1**, complete conversion of the lesser mercurated complexes to the octamercurated species does not occur, even upon extended reflux with excess mercuric acetate. This experiment suggests that exhaustive permercuration fails due to the extreme insolubility of the higher mercurated ferrocenes, rather than from steric crowding about the ferrocene skeleton. The decamercurated ruthenocene and osmocene, with greater interannular distances, can be better solvated to allow complete mercuration before the product precipitates.

Despite the potential synthetic applications that could be envisioned using permercurated ferrocenes, permercuration fails, most likely due to the extremely insoluble nature of the heavily mercurated intermediates. It is probable that long-chain alkyl groups (e.g. *n*-hexyl, *n*-octyl) substituted on the ferrocene skeleton will be required to impart enough solubility to the intermediate mercurated species to allow exhaustive mercuration.

## 4. Experimental section

### 4.1. General considerations

The mercuration reactions were performed under an atmosphere of nitrogen using Schlenk techniques.

Dichloromethane was distilled from calcium hydride. Hexane was distilled from sodium. Reagent grade 1,2-dichloroethane and acetone were used as-received. Chloroform-*d* was dried over 4 Å molecular sieves. Mercuric acetate, cupric chloride, and cupric bromide were used as received from Aldrich Chemical Co.

<sup>1</sup>H NMR and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were obtained at 500, 300, 121 or 75 MHz in chloroform-*d*. Infrared spectra were obtained using potassium bromide as the medium. Mass spectra were obtained in the electron impact mode. Elemental analyses were performed by Midwest Microlab, Indianapolis, IN. Melting points were obtained on a Haake-Buchler HBI digital melting point apparatus in sealed glass tubes and are uncorrected.

### 4.2. 1,1',2,2',3,3',4,4'-Octakis(acetoxymercurio)-5,5'-dimethylferrocene (**1**)

A 50 ml Schlenk flask was charged with 1,1'-dimethylferrocene (0.509 g, 2.38 mmol), mercuric acetate (5.953 g, 18.7 mmol), 1,2-dichloroethane (50 ml), and a stir bar and was fitted with a reflux condenser. The mixture was refluxed for 18 h. Upon cooling to ambient temperature, the solvent was removed under reduced pressure to afford a yellow solid. The solid was washed with acetone (100 ml) and water (100 ml) to remove mercury impurities. The product was dried under reduced pressure to afford **1** as a yellow powder (4.97 g, 91%): dec. range 180–210 °C; IR (KBr, cm<sup>-1</sup>)  $\nu_{\text{HgO}_2\text{CCH}_3}$  1578 (s), 1378 (m). The insolubility of **1** precluded solution NMR analyses.

Anal. Found: C, 15.72; H, 1.57. C<sub>28</sub>H<sub>30</sub>FeHg<sub>8</sub>O<sub>16</sub>. Calc.: C, 14.73; H, 1.32.

### 4.3. 1,1',2,2',3,3',4,4'-Octakis(acetoxymercurio)-5,5'-diacetylferrocene (**2**)

In a fashion similar to the preparation of **1**, 1,1'-diacetylferrocene (0.503 g, 1.86 mmol) and mercuric acetate (4.72 g, 14.8 mmol) were reacted to afford **2** as a red–orange powder (3.828 g, 88%): dec. range 200–220 °C; IR (KBr, cm<sup>-1</sup>)  $\nu_{\text{HgO}_2\text{CCH}_3}$  1570 (s), 1406 (m).

Anal. Found: C, 14.79; H, 1.43. C<sub>30</sub>H<sub>30</sub>FeHg<sub>8</sub>O<sub>18</sub>. Calc.: C, 15.40; H, 1.29.

### 4.4. Nonakis(acetoxymercurio)acetylferrocene (**3**)

In a fashion similar to the preparation of **1**, acetylferrocene (0.504 g, 2.21 mmol) and mercuric acetate (6.281 g, 19.7 mmol) were reacted to afford **3** as a red–orange powder (4.91 g, 87%): dec. pt. 210 °C; IR (KBr, cm<sup>-1</sup>)  $\nu_{\text{CpCOCH}_3}$  1691 (w),  $\nu_{\text{HgO}_2\text{CCH}_3}$  1579 (s), 1360 (m).

Anal. Found: C, 15.75; H, 1.60. C<sub>30</sub>FeH<sub>30</sub>Hg<sub>9</sub>O<sub>19</sub>. Calc.: C, 14.10; H, 1.18.

#### 4.5. 1,1',2,2',3,3',4,4'-Octakis(acetoxymercurio)-5,5'-ferrocenedicarboxylic acid (**4**)

In a fashion similar to the preparation of **1**, 1,1'-ferrocene dicarboxylic acid (0.252 g, 0.920 mmol) and mercuric acetate (2.34 g, 7.34 mmol) were reacted to afford **4** as an orange–yellow powder (1.806 g, 84%): dec. range 210–215 °C; IR (KBr,  $\text{cm}^{-1}$ )  $\nu_{\text{CO}_2\text{H}}$  3405 (br),  $\nu_{\text{HgO}_2\text{CCH}_3}$  1575 (s), 1395 (m).

Anal. Found: C, 15.57; H, 1.45.  $\text{C}_{28}\text{H}_{26}\text{FeHg}_8\text{O}_{20}$ . Calc.: C, 14.35; H, 1.12.

#### 4.6. Nonakis(acetoxymercurio)ferrocene carboxylic acid (**5**)

In a fashion similar to the preparation of **1**, ferrocene carboxylic acid (0.508 g, 2.21 mmol) and mercuric acetate (6.340 g, 19.9 mmol) were reacted to afford **5** as a yellow powder (5.32 g, 94%): dec. pt. 245 °C; IR (KBr,  $\text{cm}^{-1}$ )  $\nu_{\text{CO}_2\text{H}}$  3320 (br),  $\nu_{\text{HgO}_2\text{CCH}_3}$  1573 (s), 1395 (m).

Anal. Found: C, 14.87, H, 1.45.  $\text{C}_{29}\text{FeH}_{28}\text{Hg}_9\text{O}_{20}$ . Calc.: C, 13.62; H, 1.01.

#### 4.7. Nonakis(acetoxymercurio)ferrocene carboxaldehyde (**6**)

In a fashion similar to the preparation of **1**, ferrocene carboxaldehyde (0.503 g, 2.35 mmol) and mercuric acetate (6.750 g, 21.2 mmol) were reacted to afford **6** as a yellow powder (5.11 g, 86%): dec. pt. 250 °C; IR (KBr,  $\text{cm}^{-1}$ )  $\nu_{\text{CO}}$  1700 (w),  $\nu_{\text{HgO}_2\text{CCH}_3}$  1571 (s), 1364 (m).

Anal. Found: C, 15.36; H, 1.59.  $\text{C}_{29}\text{H}_{28}\text{FeHg}_9\text{O}_{19}$ . Calc.: C, 13.70; H, 1.11.

#### 4.8. Chlorination of **1**

A 250 ml round-bottomed flask was charged with **1** (4.489 g, 1.97 mmol), copper(II) chloride dihydrate (13.410 g, 78.7 mmol), acetone (100 ml), and a stir bar and was fitted with a reflux condenser. The mixture was refluxed for 5 h. The solvent was removed under reduced pressure to give a dark oily solid. The solid was extracted with diethyl ether (150 ml) and the extract was passed through a 3 cm plug of silica gel on a coarse glass frit. The solvent was removed under reduced pressure to give a green–yellow oily solid. The resultant solid was extracted with hexane (150 ml) and the extract was passed through a 3 cm plug of silica on a coarse glass frit to afford a bright yellow solution. Removal of the solvent under reduced pressure afforded a yellow solid (0.0869 g), which was a mixture consisting of **6** (1.9% yield, based upon **1**), **7** (6.8% yield, based upon **1**), and **8** (1.0% yield, based upon **1**). All

attempts to separate the mixture failed (e.g. by crystallization, sublimation, preparative TLC, preparative reverse-phase HPLC, preparative GLC).

Data for **7**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ) 1.92 (s,  $\text{C}_5\text{Cl}_4\text{CH}_3$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , ppm) 89.09, 89.04 (s, C–Cl), 80.18 (s, C– $\text{CH}_3$ ), 7.72 (s, C– $\text{CH}_3$ ); MS (EI, 20 eV) 490 ( $\text{M}^+$ , 16%), 109 ( $\text{C}_5\text{ClCH}_3$ , 100%), 75 ( $\text{C}_5\text{CH}_3$ , 56%).

Data for **8**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ) 4.09 (s,  $\text{C}_5\text{HCl}_3\text{CH}_3$ ), 1.96, 1.90 (s,  $\text{C}_5\text{HCl}_3\text{CH}_3$  and  $\text{C}_5\text{C}_4\text{CH}_3$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , ppm) 91.64, 91.25, 91.09, 90.00, 89.66, 89.60, 89.54 (s, C–Cl), 82.77, 79.23 (s, C– $\text{CH}_3$ ), 71.51 (s, C–H), 9.36, 8.11 (s, C– $\text{CH}_3$ ); MS (EI, 20 eV) 455 ( $\text{M}^+$ , 15%), 75 ( $\text{C}_5\text{CH}_3$ , 100%).

Data for **9**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ) 4.33 (s,  $\text{C}_5\text{HCl}_3\text{CH}_3$ ), 1.97 (s,  $\text{C}_5\text{HCl}_3\text{CH}_3$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , ppm, partial spectrum) 71.28 (s, C–H), 8.32 (s, C– $\text{CH}_3$ ); MS (EI, 20 eV) 421 ( $\text{M}^+$ , 8.5%), 75 ( $\text{C}_5\text{CH}_3$ , 100%).

#### 4.9. Bromination of **1**

A 250 ml round-bottomed flask was charged with **1** (3.83 g, 1.68 mmol), copper(II) bromide (14.995 g, 67.1 mmol), acetone (100 ml), and a stir bar and was fitted with a reflux condenser. The mixture was refluxed for 3.5 h. The solvent was removed under reduced pressure to give a green–black oily solid. The solid was extracted with hexane and the extract was passed through a 3 cm plug of silica gel on a coarse glass frit. The solvent was removed under reduced pressure to give a bright yellow powder (0.124 g), which was a mixture of **10** (2.1% yield based upon **13**), **11** (6.9% yield based upon **1**), and **12** (0.4% yield based upon **1**). Three other unidentified minor products, totaling no more than 10 mol.% of the total ferrocene mixture, were observed by  $^1\text{H}$  NMR.

Data for **10**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ) 1.92 (s,  $\text{C}_5\text{Br}_4\text{CH}_3$ ).

Data for **11**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ) 4.15 (s,  $\text{C}_5\text{HBr}_3\text{CH}_3$ ), 1.99, 1.92 (s,  $\text{C}_5\text{Br}_4\text{CH}_3$ ,  $\text{C}_5\text{HBr}_3\text{CH}_3$ ).

Data for **12**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ) 4.24 (s,  $\text{C}_5\text{HBr}_3\text{CH}_3$ ), 1.97 (s,  $\text{C}_5\text{HBr}_3\text{CH}_3$ ).

MS (EI, 20 eV, mixture of **10–12**): 845 (11%,  $(\text{C}_5\text{Br}_4\text{CH}_3)_2\text{Fe}$ ), 765 (100%,  $(\text{C}_5\text{Br}_4\text{CH}_3)(\text{C}_5\text{HBr}_3\text{CH}_3)\text{Fe}$ ), 687 (2.0%,  $(\text{C}_5\text{HBr}_3\text{CH}_3)_2\text{Fe}$ ).

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