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Notes

Functionalization of $Cp_4Fe_4(CO)_4$ with Alkyl, Aryl, and Ferrocenyl Groups and the Preparation of Double Clusters $[Cp_3Fe_4(CO)_4(C_5H_4)]_2$ and $[Cp_3Fe_4(CO)_4(C_5H_4)]_2[(C_5H_4)_2Fe]$

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*Summary: Reaction of $Cp_4Fe_4(CO)_4$ (**1**) with RLi and HBF_4 in sequence affords $Cp_3Fe_4(CO)_4(C_5H_4R)$ (R= Me, Bu^n, and Ph) in moderate yields. Further sequential PhLi/HBF_4 treatment of $Cp_3Fe_4(CO)_4(C_5H_4Ph)$ produces $Cp_2Fe_4(CO)_4(C_5H_4Ph)_2$. On the other hand, **1** reacts with lithium diisopropylamide (LDA) and bromoferrocene sequentially to produce a ferrocenylated cluster $[Cp_3Fe_4(CO)_4(C_5H_4)][(C_5H_4)FeCp]$ (**3**) and a double cluster $[Cp_3Fe_4(CO)_4(C_5H_4)]_2$ (**2**). A similar LDA/dibromoferrocene treatment with **1** leads to **2**, $[Cp_3Fe_4(CO)_4(C_5H_4)][(C_5H_4)(C_5H_4Br)Fe]$ (**4**), and a ferrocenyl-bridged double cluster $[Cp_3Fe_4(CO)_4(C_5H_4)]_2[(C_5H_4)_2Fe]$ (**5**). The new compounds have been characterized by elemental analysis and IR, mass, and NMR spectroscopy.*

Introduction

The study of transition metal clusters is currently a very active area of chemical research.[1] The interest in cluster compounds transcends their synthesis and unique structural features. In addition, discrete, soluble metal clusters often display catalytic activity[2] and are studied as models for the surface of bulk metals.[3] $Cp_4Fe_4(CO)_4$ (**1**), originally reported by King,[4] is one of the first substances containing a tetrahedral cluster of metal atoms. A unique feature of this stable cluster is that it is electroactive, reversibly undergoing both reduction and oxidation,[5] which property is essential to perform important functions such as solar energy conversion and multielectron catalysis.[6] Since its discovery, compound **1** has been the subject of numerous research papers.[7−13] Recently, Rauchfuss and co-workers reported[14,15] functionalization of **1** to give $Cp_3Fe_4(CO)_4(C_5H_4R)$ (R = Bu, Ph, $C(OH)HCH_3$, CO_2H, CHO, SPh, and PPh_2, etc.). We have been independently investigating the substitution reactions of **1** for many years.[16] Presented in this note are new derivatives of **1** containing alkyl, aryl, and ferrocenyl substituents on the cyclopentadienyl ligands as well as two novel double-clusters $[Cp_3Fe_4(CO)_4(C_5H_4)]_2$ and $[Cp_3Fe_4(CO)_4(C_5H_4)]_2[(C_5H_4)_2Fe]$.

Experimental Section

All manipulations were carried out under an atmosphere of purified dinitrogen with standard Schlenk techniques.[17] $Cp_2Fe_2(CO)_4$,[18] bis(diphenylphosphino)ferrocene,[19] bromoferrocene,[20] and 1,1′-dibromoferrocene[21] were prepared by literature meth-

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ods. Lithium diisopropylamide (LDA, 1.5 M in cyclohexane), *n*-butyllithium (15% in *n*-hexane), methyllithium (1.4 M in ether), phenyllithium (1.8 M, in cyclohexane−ether), tetrafluoroboric acid (85%, ether complex), and triphenylphosphine were purchased from Aldrich and used as received. Solvents were dried over appropriate reagents under dinitrogen and distilled immediately before use. Preparative thin-layer chromatographic (TLC) plates were prepared from silica gel (Merck). Infrared spectra were recorded with a 0.1 mm path CaF_2 solution cell on a Hitachi I-2001 IR spectrometer. ^1H and ^{13}C NMR spectra were obtained on a Varian VXR-300 spectrometer at 300 and 75.4 MHz, respectively. Fast-atom-bombardment (FAB) mass spectra were recorded by using a VG Blotch-5022 mass spectrometer. Elemental analyses were performed at the National Science Council Regional Instrumentation Center at National Chen-Kung University, Tainan, Taiwan.

Alternative Synthesis of 1. $Cp_2Fe_2(CO)_4$ (100 mg, 0.28 mmol), bis(diphenylphosphino)ferrocene (dppf, 188 mg, 0,34 mmol), and toluene (10 mL) were placed in a 100 mL Schlenk flask. The mixture was heated to reflux under N_2 for 10 h and cooled to ambient temperature. The solvent was removed under vacuum and the residue subjected to TLC, eluting with dichloromethane. The first yellow band recovered dppf in 90% yield. Isolation of the material forming the second green band afforded $Cp_3Fe_4(CO)_4(C_5H_4Ph)$ (**1Ph**, 15 mg, 0.022 mmol, 16% based on the Fe atoms). The third green band gave $Cp_4Fe_4(CO)_4$ (**1**, 60 mg, 0.1 mmol, 71%).

1Ph. Mass spectrum (FAB): *m*/*z* 672 (M^+, ^{56}Fe) 613, 596, 495, 460, 443, 419. IR (C_6H_6): ν(CO) 1644 cm^{-1}. ^1H NMR ($CDCl_3$, 20 °C): δ 7.78−7.23 (m, Ph), 5.01 (t, 2H, C_5H_4), 4.84 (t, 2H, C_5H_4), 4.54 (s, 15H, Cp).

1. Mass spectrum (FAB): *m*/*z* 596 (M^+, ^{56}Fe), 419. IR (C_6H_6): ν(CO) 1644 cm^{-1}. ^1H NMR ($CDCl_3$, 20 °C): δ 4.77 (s, Cp).

Sequential RLi/HBF$_4$ Treatment of 1. Typically, an oven-dried, 100 mL Schlenk flask was charged with $Cp_4Fe_4(CO)_4$ (**1**) (50 mg, 0.084 mmol) and THF (5 mL) under N_2. The flask was placed in an ice bath, and PhLi (0.42 mmol) was slowly introduced by a microsyringe, forming a yellow-green solution. A methanol (2 mL) solution of HBF_4 (100 μL) was then introduced into the flask, and the mixture was stirred at 0 °C for 1 h. The volatile materials were removed under vacuum and the residue separated by TLC, eluting with *n*-hexane−dichloromethane−ethyl acetate (3:1:1, v/v). The first and second green bands gave **1Ph** and unreacted **1** in 55% and 14% yield, respectively. Further PhLi/HBF_4 treatment of **1Ph** in an identical fashion led to **1Ph$_2$** in 41% yield.

Likewise, sequential MeLi/HBF_4 and BuLi/HBF_4 treatments of **1** afforded $Cp_3Fe_4(CO)_4(C_5H_4Me)$ (**1Me**, 40%) and ($Cp_3Fe_4(CO)_4(C_5H_4Bu^n)$) (**1Bu**, 52%), respectively, together with unreacted **1**.

1Ph$_2$. Mass spectrum (FAB): *m*/*z* 748 (M^+, ^{56}Fe), 718, 647, 571, 495. IR (CH_2Cl_2): ν(CO) 1640 cm^{-1}. ^1H NMR ($CDCl_3$, 20 °C): δ 7.78−7.23 (m, Ph), 4.89 (t, 2H, C_5H_4), 4.67 (t, 2H, C_5H_4), 4.32 (s, 10H, Cp). Anal. Calcd for $C_{36}H_{28}O_4Fe_4$: C, 57.75; H, 3.74. Found: C, 57.32; H, 3.70.

1Me. Mass spectrum (FAB): *m*/*z* 610 (M^+, ^{56}Fe), 596, 433, 419. IR (THF): ν(CO) 1644 cm^{-1}. ^1H NMR ($CDCl_3$, 20 °C): δ 4.72 (s, 15H, Cp), 4.65 (t, 2H, C_5H_4), 4.39 (t, 2H, C_5H_4), 2.05 (s, 3H, Me). Anal. Calcd for $C_{25}H_{22}O_4Fe_4$: C, 49.18; H, 3.60. Found: C, 49.48; H, 3.57.

1Bu. Mass spectrum (FAB): *m*/*z* 652 (M^+, ^{56}Fe), 624, 596, 475, 419. IR (THF): ν(CO) 1648 cm^{-1}. ^1H NMR (acetone-*d*$_6$, 20 °C):δ 4.66 (s, 15H, Cp), 4.59 (t, 2H, C_5H_4), 4.40 (t, 2H, C_5H_4), 2.54 (t, 2H, Bu). 1.55−1.20 (m, 4H, Bu), 0.85 (t, 3H, Bu).

Sequential LiNPr$^i_2$/(C$_5$H$_4$Br)FeCp Treatment of 1. An oven-dried, 100 mL Schlenk flask was charged with $Cp_4Fe_4(CO)_4$ (**1**) (300 mg, 0.50 mmol) and freshly distilled diethyl ether (30 mL) and THF (10 mL) under a dinitrogen atmosphere. The flask was placed in an ice bath, and lithium diisopropylamide (LDA, 1.34 mL, 2.01 mmol) was added via an airtight syringe. The flask was then removed from the ice bath, and the mixture was stirred at room temperature for 10 h, forming a dark green precipitate. The supernatant was discarded, and the precipitate was washed with diethyl ether and dried under vacuum. A solution of bromoferrocene (132 mg, 0.5 mmol) in THF (10 mL) was introduced, and the flask was placed in an oil bath at 45−50 °C for 22 h. The solvent was then removed on a rotary evaporator, and the residue was subjected to TLC, eluting with ethyl acetate−dichloromethane−*n*-hexane (1:1:3, v/v). The first band was the unreacted bromoferrocene. The second band was $Cp_2Fe_2(CO)_4$ (5%). The third band afforded $[Cp_3Fe_4(CO)_4(C_5H_4)][(C_5H_4)FeCp]$ (**3**) (90 mg, 23%). The fourth band recovered the starting material **1** in 33% yield. The materials after the fourth band were collected and separated again by TLC, with ethyl acetate−dichloromethane (3:1, v/v) as eluant. The second band afforded $[Cp_3Fe_4(CO)_4(C_5H_4)]_2$ (**2**) (17 mg, 6%). The remaining several bands were not characterized.

Compounds **2** and **3** were recrystallized from dichloromethane−hexane at −20 °C to give dark green, air-stable microcrystalline solids.

2. Mass spectrum (FAB): *m*/*z* 1190 (M^+, ^{56}Fe). IR (CH_2Cl_2): ν(CO) 1640 cm^{-1}. ^1H NMR (acetone-*d*$_6$, 25 °C): δ 4.83 (s, 30H, Cp), 4.78 (t, J_{H-H} = 2 Hz, 4H, C_5H_4), 4.68 (t, J_{H-H} = 2 Hz, 4H, C_5H_4). Anal. Calcd for $C_{48}H_{38}O_8Fe_8$: C, 48.41; H, 3.22. Found: C, 48.09; H, 3.10.

3: Mass spectrum (FAB): *m*/*z* 780 (M^+, ^{56}Fe). IR (CH_2Cl_2): ν(CO) 1637 cm^{-1}. ^1H NMR (C_6D_6, 25 °C): δ 4.80 (t, J_{H-H} = 2 Hz, 2H, $C_5H_4-Fe_4$), 4.73 (t, J_{H-H} = 2 Hz, 2H, $C_5H_4-Fe_4$), 4.59 (s, 15H, Cp_3Fe_4), 4.48 (t, J_{H-H} = 2 Hz, 2H, C_5H_4Fe), 4.10 (t, J_{H-H} = 2 Hz, 2H, C_5H_4Fe), 3.89 (s, 5H, CpFe). Anal. Calcd for $C_{34}H_{28}O_4Fe_5$: C, 52.37; H, 3.62. Found: C, 52.47; H, 3.61.

Sequential LiNPr$^i_2$/(C$_5$H$_4$Br)$_2$Fe Treatment of 1. $Cp_4Fe_4(CO)_4$ (**1**) (250 mg, 0.42 mmol) was sequentially treated with LDA (1.1 mL, 0.92 mmol) and dibromoferrocene (200 mg, 0.58 mmol) in a fashion identical with that above. The reaction mixture was subjected to TLC, eluting with ethyl acetate−dichloromethane−*n*-hexane (1:1:3, v/v). The first band was the unreacted dibromoferrocene. The second band was $[CpFe(CO)_2]_2$ (2%). The third band afforded $[Cp_3Fe_4(CO)_4(C_5H_4)][(C_5H_4)(C_5H_4Br)Fe]$ (**4**) (63 mg, 18%). The fourth band recovered **1** (109 mg, 44%). The fifth band yielded $[Cp_3Fe_4(CO)_4(C_5H_4)]_2[(C_5H_4)_2Fe]$ (**5**) (23 mg, 8%). The materials remaining on the TLC plates were extracted with methanol and purified again by TLC, with ethyl acetate−dichloromethane (3:1, v/v) as eluant. The second band afforded compound **2** (12 mg, 5%). The several other bands were not characterized.

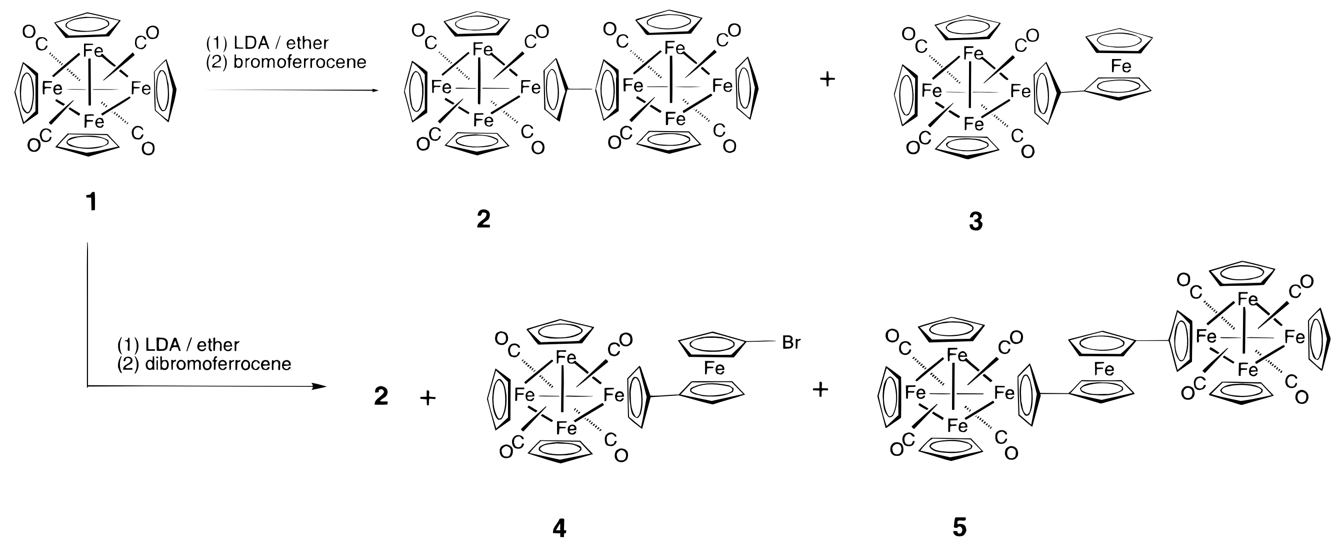
4. Mass spectrum (FAB): *m*/*z* 858 (M^+, ^{56}Fe, ^{79}Br). IR (CH_2Cl_2): ν(CO) 1638 cm^{-1}. ^1H NMR (C_6D_6, 25 °C): δ 4.76 (t, J_{H-H} = 2 Hz, 2H, $C_5H_4-Fe_4$), 4.73 (t, J_{H-H} = 2 Hz, 2H, $C_5H_4-Fe_4$), 4.63 (t, J_{H-H}= 2 Hz, 2H, C_5H_4-Fe),4.58 (s, 15H, Cp), 4.08 (t, J_{H-H} = 2 Hz, 2H, C_5H_4-Fe), 4.06 (t, J_{H-H} = 2 Hz, 2H, C_5H_4-Br), 3.62 (t, J_{H-H} = 2 Hz, 2H, C_5H_4Br). $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C): δ 290 (CO), 289 (CO), 105.9, 94.7, 99.5, 72.4, 72.1, 70.4, 69.0 (Cp). Anal. Calcd for $C_{34}H_{27}O_4BrFe_5$: C, 47.56; H, 3.17. Found: C, 47.44; H, 3.16.

5. Mass spectrum (FAB): *m*/*z* 1374 (M^+, ^{56}Fe). IR (CH_2Cl_2): ν(CO) 1640 cm^{-1}. ^1H NMR (C_6D_6, 25 °C): δ 4.86 (dd, J_{H-H} = 2 Hz, 4H, $C_5H_4-Fe_4$), 4.79 (dd, J_{H-H} = 2 Hz, 4H, $C_5H_4-Fe_4$), 4.74 (s, 30H, Cp), 4.50 (dd, J_{H-H} = 2 Hz, 4H, C_5H_4-Fe), 4.22 (dd, J_{H-H} = 2 Hz, 4H, C_5H_4-Fe). Anal. Calcd for $C_{58}H_{46}O_8Fe_9$: C, 50.72; H, 3.38. Found: C, 50.74; H, 3.45.

Results and Discussion

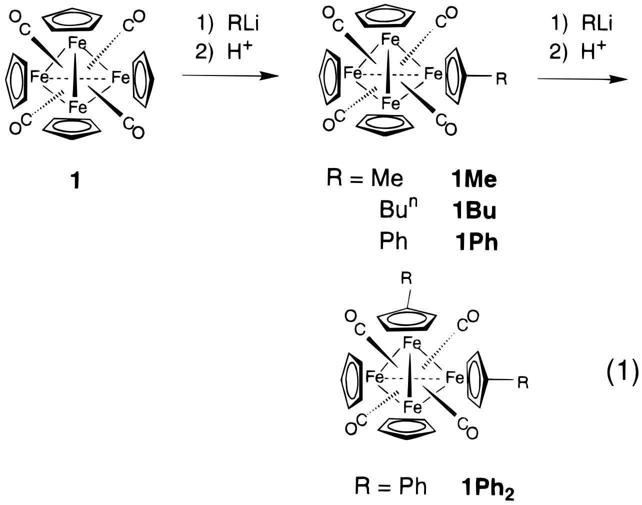
Synthesis. $Cp_4Fe_4(CO)_4$ (**1**, 71%) and $Cp_3Fe_4(CO)_4(C_5H_4Ph)$ (**1Ph**, 16%) have been obtained from thermolysis of $[CpFe(CO)_2]_2$ and bis(diphenylphosphino)ferrocene in refluxing toluene for 10 h. King[4] originally prepared **1** in 14% yield by heating $[CpFe(CO)_2]_2$ in

Scheme 1



reluxing xylene for 14 days. A modified method described by White[22] was to heat $[CpFe(CO)_2]_2$ and PPh_3 in refluxing xylene to give **1** in 56% yield, whereas Rauchfuss[14] carried out the same reaction to obtain **1** (27%), **1Ph** (3%), and a triiron cluster $Cp_3Fe_3(CO)_3(PPh_2)$ (1%). Rheingold[23] prepared **1** in nearly 80% yield by carrying out the above reaction under UV irradiation. The discovery of **1Ph** by Rauchfuss is novel because it was totally unsuspected in the previous reports. The origin of the phenyl substituent in **1Ph** is not certain, presumably from fragmentation of the phosphine coreactant.

Reaction of **1** and RLi in THF at 0 °C followed by acidification with HBF_4 affords $Cp_3Fe_4(CO)_4(C_5H_4R)$ in 40%, 52%, and 55% yields for R = Me (**1Me**), Bu^n (**1Bu**), and Ph (**1Ph**), respectively. Further Ph^-/H^+ treatment of **1Ph** affords **1Ph$_2$** in 41% yield (eq 1). Rauchfuss and



(1)

co-workers recently showed the reactions of **1** with Bu^{n}Li and PhLi at −40 °C, following by adding Ph_2S_2 and workup in air, to afford **1Bu** (44%) and **1Ph** (5%).[14] In the latter reaction, the low yield of **1Ph** was attributed to reduction which competes with nucleophilic addition at low temperature.

To figure out if deprotonation reaction occurs in the above reactions, compound **1** was successively treated with Bu^{n}Li and bromoferrocene. The reaction mixture after separation by TLC leads to mainly unreacted **1** (20%) and **1Bu** (24%) and a ferrocenylated product $[Cp_3Fe_4(CO)_4(C_5H_4)][(C_5H_4)FeCp]$ (**3**) in 9% yield. Apparently, the alkyl- and aryllithium reagents are capable of functioning as a nucleophile, reducing agent, and base in their reactions with **1**.

It becomes clear that a strong base of poor nucleophilicity, such as lithium diisopropylamide (LDA) or lithium tetramethylpiperidide (LTMP),[24] should facilitate the deprotonation reaction. Thus, sequential treatment of $Cp_4Fe_4(CO)_4$ (**1**) with LDA and bromoferrocene significantly increases the yield of **3** (23%) together with a novel fulvalenyl-bridged double cluster $[Cp_3Fe_4(CO)_4(C_5H_4)]_2$ (**2**, 6%) and several uncharacterized products. A similar reaction, but replacing bromoferrocene by dibromoferrocene, affords **2** (5%), $[Cp_3Fe_4(CO)_4(C_5H_4)][(C_5H_4)(C_5H_4Br)Fe]$ (**4**, 18%), and a ferrocenyl-bridged double cluster $[Cp_3Fe_4(CO)_4(C_5H_4)]_2[(C_5H_4)_2Fe]$ (**5**, 8%). The results are summarized in Scheme 1. In both reactions, **1** is recovered in 33−45% yield even though the reactions monitored by IR show no presence of **1** after introduction of LDA. Presumably, reduction of **1** competes with deprotonation reaction here and limits the utility of the LDA reagent.

The use of LDA as a nonnucleophilic base, previously shown by Rauchfuss[14] on the functionalization of **1**, is a unique method because LDA is not commonly employed to metalate Cp ligands.[25] Moreover, nucleophilic displacement of the bromide atom from ferrocene derivatives by $[Cp_3Fe_4(CO)_4(C_5H_4)]^-$ anion to generate **3**−**5** is an unusual reaction. It is normally the $[CpFe(C_5H_4)]^-$ and $[Fe(C_5H_4)_2]^{2-}$ anions prepared from bromoferrocene and ferrocene that react with electrophiles, such as acyl halides and aldehydes, on the functionalization of ferrocene.[26] Finally, the formation of **2** is noted. It is

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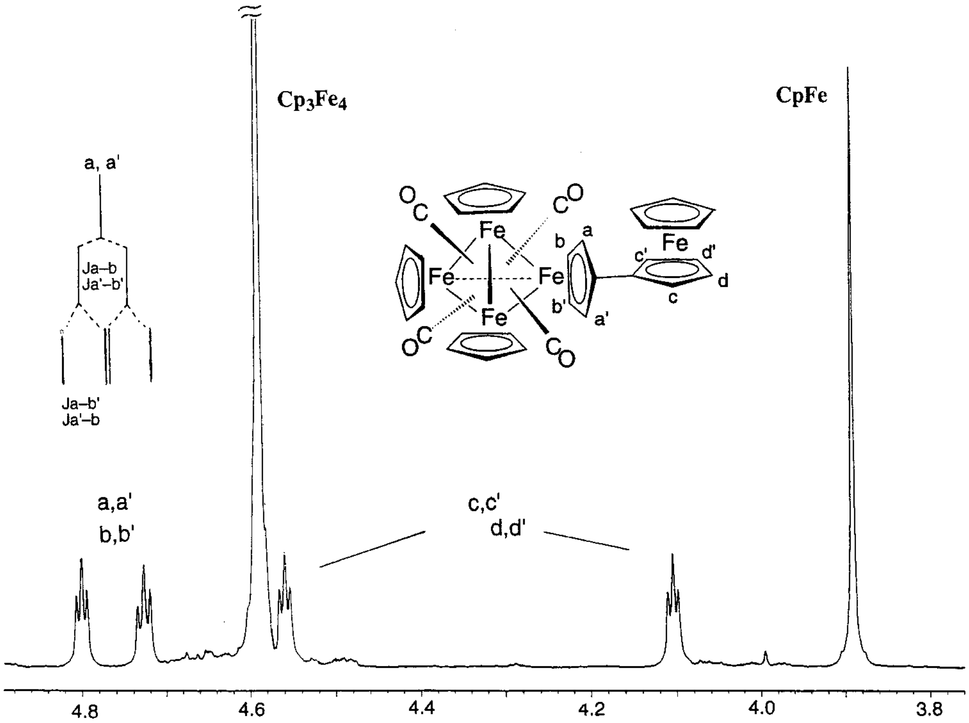

Figure 1. 300 MHz ^{1}H NMR spectrum of compound **3** obtained in C_6D_6 at 25 °C.

likely that $[Cp_3Fe_4(CO)_4(C_5H_4)]^-$ attacks **1** to afford the intermediate $[(Cp_3Fe_4(CO)_4)_2(C_5H_4{-}C_5H_5)]^-$, followed by dehydration, which leads to **2**.

Spectroscopic Characterization of New Compounds. The spectroscopic data of **1Ph** and **1Bu** closely agree with those recently reported by Rauchfuss and co-workers.[14] The new compounds **1Me**, **1Ph$_2$**, and **2**−**5** give satisfactory C, H elemental analyses and have been characterized by mass, IR, and NMR spectroscopy.

Compounds **1Ph$_2$** and **1Me** form air-stable, green crystalline solids. The FAB mass spectrum of **1Me** presents the molecular ion peak at *m*/*z* 610, and **1Ph$_2$** at *m*/*z* 748. The ^{1}H NMR of **1Me** shows two singlets at δ 2.05 and 4.71 for the Me and Cp protons and two pseudo-triplets in equal intensity at δ 4.39 and 4.65 for the C_5H_4 group. The ^{1}H NMR pattern of **1Ph$_2$** is identical with that of **1Ph**, clearly indicating that the two phenyl substituents are located on different cyclopentadienyl groups.

The FAB mass spectra of **2**−**5** display their molecular ion peaks at *m*/*z* 1190, 780, 858, and 1374, respectively, for ^{56}Fe and ^{79}Br isotopes. The isotopic distribution of the envelope surrounding the molecular ions matches that expected for these compounds, and there is good agreement between the calculated mass distribution and the observed mass spectra. The IR spectra of these compounds in the carbonyl region present one broad absorption at 1640 cm^{-1} for the triply bridging carbonyl ligands, suggesting that their tetrahedral iron cores remain intact.

The ^{1}H NMR spectra of **2**−**5** are closely related, where the unsubstituted Cp groups coordinated to the Fe_4 cluster display a singlet resonance and each substituted C_5H_4 group shows two sets of multiplet resonances, consistent with a molecule of idealized C_s symmetry in solution. The ^{1}H NMR spectrum of **3** is illustrated in Figure 1. The sharp singlets at δ 4.59 and 3.89 in a 3:1 ratio are attributed to the Cp_3Fe_4 and CpFe groups, respectively, while the triplet signals at δ 4.80 and 4.73 are assigned to the $C_5H_4Fe_4$ protons and the triplet signals at δ 4.48 and 4.10 to the C_5H_4Fe protons. The pseudo-triplet pattern apparently rises from overlap of a doublet of doublets, where each *ortho* proton is coupled with two magnetically nonequivalent *meta* protons and vice versa.

Conclusions

Several novel iron clusters, with the metal nuclearity of 4, 5, 8, and 9, have been prepared from **1** through functionalization of the Cp rings with methyl, butyl, phenyl, ferrocenyl, and $Cp_3Fe_4(CO)_4(C_5H_4)$ groups. Compound **1** is susceptible to nucleophilic addition, deprotonation, and reduction, depending on the nucleophilicity/basicity of the organolithium reagents and the reaction conditions. Preliminary cyclic voltammetric study of these compounds shows interesting, but complicated results. Efforts to isolate the oxidized/reduced species of **2**−**5** through chemical redox methods as well as investigation of their electrochemical properties are currently undertaken.

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