Metallocene Complexes of Iron and Cobalt Derived from the 4,4′-Bis(η^5-cyclopentadienyl)octafluorobiphenyl Ligand[1]

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The reaction of decafluorobiphenyl with 10 equiv of sodium cyclopentadienide (NaCp) in THF (65 °C, 2 h) afforded 4,4′-bis(cyclopentadienyl)octafluorobiphenyl (**1**) as a mixture of double-bond isomers in 72% yield after workup and purification. Subsequent treatment with sodium hydride in THF (25 °C, 6 h) afforded disodium 4,4′-bis(cyclopentadienyl)octafluorobiphenyl (**2**). Reaction of NaCp, ligand **2**, and $FeBr_2$ (21:1:10 mol ratio) in THF afforded mostly ferrocene as well as the diiron complex $CpFe(\eta^5\text{-}C_5H_4\text{-}4,4'\text{-}C_6F_4C_6F_4\text{-}\eta^5\text{-}C_5H_4)FeCp$ (**3**), the linear triiron complex $Cp[Fe(\eta^5\text{-}C_5H_4\text{-}4,4'\text{-}C_6F_4C_6F_4\text{-}\eta^5\text{-}C_5H_4)]_2FeCp$ (**4**), and the linear tetrairon complex $Cp[Fe(\eta^5\text{-}C_5H_4\text{-}4,4'\text{-}C_6F_4C_6F_4\text{-}\eta^5\text{-}C_5H_4)]_3FeCp$ (**5**), which were isolated by liquid chromatography. Solution voltammetric analysis of **3** showed a single, reversible two-electron oxidation at +200 mV, **4** showed two reversible oxidations (2:1 ratio) at +180 and +372 mV, respectively, and **5** showed two reversible oxidations (2:2 ratio) at +192 and +382 mV, respectively (all vs $Cp_2Fe|Cp_2Fe^+$). A similar reaction of NaCp, ligand **2**, and $CoBr_2$ in THF was worked up with air and dilute aqueous HCl followed by aqueous KPF_6 to afford a mixture of cobaltocenium hexafluorophosphates, from which $[Cp_2Co]^+PF_6^-$ and the dicobalt complex $[CpCo(\eta^5\text{-}C_5H_4\text{-}4,4'\text{-}C_6F_4C_6F_4\text{-}\eta^5\text{-}C_5H_4)CoCp]^{2+}[PF_6^-]_2$ (**6**) were isolated by liquid chromatography. CV analysis of **6** showed a single, reversible $Co^{II}|Co^{III}$ wave at +232 mV relative to $Cp_2Co|Cp_2Co^+$. These voltammetric data suggest that no significant electronic communication exists between two metals bridged by this conjugated dibasic ligand (**2**). A crystal structure of diiron complex **3** demonstrated the conformational preferences of the $CpC_6F_4C_6F_4Cp$ ligand in the solid state with respective torsional angles of 37.5°, 50.1°, and 32.1°.

Introduction

Steady interest in the synthesis of multimetallic complexes derived from redox-active transition-metal complexes is evident in the recent literature. Ferrocene-containing polymers in which the complexed iron atoms are integral to the principal chain have received the most attention.[4] The application of the $Fe^{II}|Fe^{III}$ couple as a charge carrier in conducting organic filaments or films is among the long-range objectives of that research. For this reason, homobimetallic complexes in which two ferrocene units are linked by simple organic spacers serve as important benchmarks for the optimization of synthetic methods and for the investigation of intramolecular (intrachain) communication among the covalently linked ferrocene units.

Most synthetic approaches to oligoferrocenes are based on coupling, condensation, or ring-opening reactions of functional substituents attached to the ferrocene core.[5] The step-growth oligomerization of metal halides such as $FeCl_2$ with "dibasic" ligands (having two tethered cyclopentadienyl groups) is somewhat less common, partly because molecular weight and end group functionality are difficult to control.[6] Yet, the persistent advantage of the dibasic ligand approach is flexibility with respect to the tethering group between the ligands as well as the transition metals and ligated metal fragments that can be coordinated.

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We now report the synthesis of a dibasic ligand (**2**) in which two cyclopentadienyl anions are tethered by the rigid-rod-shaped 4,4′-octafluorobiphenylene moiety. Arylene groups are chemically stable yet fully conjugated, improving the possibility of intermetallic electronic communication.[7] Using this "dibasic" ligand in conjunction with a large excess of the unsubstituted Cp anion as an added chain-end "capping" reagent, we obtained homobimetallic complexes of the type CpMCp-tether-CpMCp, where M = Co(+) and Fe and the tether is 4,4′-octafluorobiphenylene. The diiron complex **3** was analyzed by solution voltammetry and structurally characterized by single-crystal X-ray diffraction. Triiron and tetrairon complexes having the general formula CpFe[Cp-tether-CpFe]$_n$Cp (n = 2, 3) were also isolated.

Experimental Section

General Considerations. All reactions were carried out using routine inert-atmosphere techniques. NMR spectra were recorded on either a Varian U-400 or a Bruker AM-360 instrument. Carbon NMR spectra were referenced to the solvent,[8] proton NMR spectra were referenced to residual solvent isotopomers,[8] and fluorine NMR spectra were referenced to external C_6F_6 in $CDCl_3$ (−163.0 ppm). High-resolution mass spectrometric analyses were performed by the Nebraska Center for Mass Spectrometry (Lincoln, NE), under fast-atom bombardment conditions using a 3-nitrobenzoic acid matrix and analyzing for positive ions. Elemental microanalysis was performed by Oneida Research Services (Whitesboro, NY) or Desert Analytics (Tucson, AZ). Solvents were purified by established methods.[9] $FeBr_2$ and KPF_6 were used as received from Aldrich. $CoBr_2$ was prepared from the commercial hydrate (Fisher) by drying for several hours under vacuum at 150 °C to afford a bright green powder. Decafluorobiphenyl was used as received from Lancaster.

Crystallographic Studies. A red needle of the diiron complex **3**, grown by slow evaporation of a hexanes solution, was attached to a glass fiber with epoxy and mounted on the goniometer of a Siemens (Bruker) P4 diffractometer. Unit cell parameters were determined by least-squares refinement of 40 reflections that had been automatically centered on the diffractometer.[10] Intensity data were collected, processed,[10] and corrected for absorption.[11] The structure was solved by direct methods and refined using the SHELXTL-PC v5.03 program package.[11] The Laue symmetry and systematic absences were consistent with the monoclinic space group $P2_1/c$. Hydrogen atoms were refined independently using an anisotropic model. The program package SHELXTL-PC was used for the ensuing molecular graphics generation.[11] Data collection and structure refinement information for complex **3** is summarized in Table 1.

Electrochemical Measurements. Single-sweep cyclic and Osteryoung square wave voltammetric data were obtained for the sparingly soluble substituted ferrocenes **3**−**5** at nominal concentrations roughly estimated to be about 2 μM in CH_2Cl_2 using 0.10 M [n-Bu_4N][PF_6] as the electrolyte and activated alumina as an internal desiccant. The analyses of cobaltocenium hexafluorophosphates were carried out in a similar manner, using acetonitrile as the solvent. The apparatus was a BioAnalytical Systems BAS-100B automated digital potentiostat with a Pt disk working electrode, a Pt wire auxiliary electrode, and a Ag/AgCl reference electrode. Cyclic voltammetric (CV) sweeps for substituted ferrocenes were typically initialized at +100 mV, scanned to +1100 mV, and reversed to +100 mV, at a scan rate of 100 mV s^{-1}. CV sweeps for substituted cobaltocenium hexafluorophosphates were typically initialized at −100 mV, scanned to −1300 mV, and reversed to −100 mV, at a scan rate of 100 mV s^{-1}. $|E_{ox} - E_{red}|$ were less than 70 mV, and I_c/I_a was within 10% of unity, both indicators of well-behaved, substantially reversible couples.

Table 1. Crystallographic Data for the Diiron Complex (3)

empirical formula	$C_{32}H_{18}F_8Fe_2$
fw	666.16
diffractometer	Siemens P4
cryst dimens (mm)	0.4 × 0.4 × 0.08
color, habit	red, rod
cryst system	monoclinic
a (Å)	7.593(2)
b (Å)	18.420(8)
c (Å)	18.428(3)
β (deg)	101.88(2)
V (Å)^3	2522.2(9)
space group	$P2_1/c$ (No. 14)
Z	4
D_{calc} (Mg m^{-3})	1.754
n	1.232
F_{000}	1336
λ (Mo Kα, graphite) (Å)	0.71073
temp (K)	298(2)
θ range for collection (deg)	1.58−25.99
no. of reflns colld	6532
no. of indep reflns	4971
abs corr method	integration
max, min transm	0.7351, 0.6910
no. of data/restrts/params	4969/0/451
R indices (all data)	R1 = 0.0678, wR2 = 0.1003
final R indices [$I > 2\sigma(I)$]	R1 = 0.0385, wR2 = 0.0883
GoF on F^2	1.079
largest diff peak and hole (e Å^{-3})	0.406, −0.475

Table 2. Electrochemical Data for Complexes 3−6

complex	M^{II}/M^{III} oxidation potential, mV[a]
3	+200(5)[b]
4	+180(5), +372(5) (2:1 ratio)[b]
5	+192(5), +382(5) (1:1 ratio)[b]
$(C_6F_5Cp)_2Fe$	+346(5)[b,c]
6	+232(5)[d]
$[(C_6F_5Cp)_2Co]^+$	+400(5)[d,e]

[a] Standard errors in parentheses. [b] Relative to $[Cp_2Fe]/[Cp_2Fe]^+$ in dichloromethane. [c] Data from ref 12. [d] Relative to $[Cp_2Co]/[Cp_2Co]^+$ in acetonitrile. Values relative to $[Cp_2Fe]/[Cp_2Fe]^+$ may be obtained by subtracting 1320 mV, as the oxidation potentials of Cp_2Co and Cp_2Fe were reported to be −910 and +410 mV vs SCE, respectively, in acetonitrile (see ref 21a−c). [e] Data from ref 16.

Shifts in oxidation potential of substituted ferrocenes relative to internal Cp_2Fe were obtained by Osteryoung square wave voltammetry (OSWV). The cell voltage was typically swept from −200 to +1100 mV with a step resolution of 4 mV, a square wave amplitude of 25 mV, and a frequency of 15 Hz for a total of 256 data points. Shifts in reduction potential of substituted cobaltocenium hexafluorophosphates relative to Cp_2Co^+ were similarly determined by OSWV using a sweep from −100 to −1300 mV. Internal resistance compensation was applied to all voltammetric experiments. Electrochemical potentials obtained by OSWV are collected in Table 2.

4,4′-Bis(cyclopentadienyl)octafluorobiphenyl (1). To a stirred mixture of sodium cyclopentadienide (8.8 g, 0.10 mol), sodium hydride (1.2 g, 0.050 mol), and THF (200 mL) was added decafluorobiphenyl (4.0 g, 0.012 mol) in one portion; gas

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evolved. The mixture was stirred at ambient temperature for 15 min and then under reflux for 2 h. The resulting dark brown mixture was cooled, and the solvent was removed under reduced pressure. The brown residue was taken up in benzene (300 mL) and hydrolyzed under a strong counterstream of nitrogen by cautious addition of water (100 mL), during which gas evolved vigorously. The biphasic mixture was stirred for 0.5 h to ensure complete hydrolysis, suction-filtered through Celite, and then separated. The aqueous layer was extracted with 100 mL of hexanes. The organic layers were combined, washed with water (3 × 50 mL), dried over anhydrous magnesium sulfate, filtered, and evaporated to afford 5.0 g (0.012 mol, 98%) of a yellow residue. Trituration with pentane (2 × 10 mL) afforded 3.7 g (8.7 mmol, 72%) of an off-white solid. ^{1}H NMR and ^{19}F NMR ($CDCl_3$) confirmed the pure product as a mixture of cyclopentadiene double-bond isomers. The ratio of double-bond isomers obtained in individual experiments varies but is typically 90:10. Major isomer: ^{1}H NMR δ 3.62 (s, 2 H), 6.73 (s, 2 H), 7.48 (m, 1 H) and ^{19}F NMR δ −141.26 (m, 4 F), −141.72 (m, 4 F). Minor isomer: ^{1}H NMR δ 3.38 (s, 2 H), 6.63 (m, 1 H), 6.91 (m, 1 H), 7.01 (m, 1 H) and ^{19}F NMR δ −140.70 (m, 4 F), −142.15 (m, 4 F). Anal. Calcd for $C_{22}H_{10}F_8$: C, 61.96; H, 2.37. Found: C, 62.19; H, 2.12.

[4,4′-Bis(cyclopentadienyl)octafluorobiphenyl]diyldisodium (2). A mixture of neutral ligand (**1**, 3.1 g, 7.3 mmol), NaH (2.0 g, 83 mmol), and THF (200 mL) was stirred at 25 °C for 6 h. Unreacted NaH was removed by filtration, and the filtrate was evaporated. The resulting orange residue was dried under vacuum (50 °C, 0.05 Torr) for 12 h, washed with pentane (100 mL), collected on a filter, and dried under vacuum to afford 3.3 g (7.0 mmol, 96%) of a bright yellow solid. ^{1}H NMR (THF-d_8): δ 6.59 (m, 4 H), 5.98 (t, $J = 2.9$ Hz, 4 H); residual THF was observed, for which reason combustion microanalysis was not attempted. ^{19}F NMR (THF-d_8): δ −143.2 (m, 4 F), −144.7 (m, 4 F); broad, unassigned resonances accounted for about 10% of the integrated signal. $\{^1H\}^{13}C$ NMR (THF-d_8): δ 148.6 (d, $^1J_{CF} = 240$ Hz, CF), 146.4 (d, $^1J_{CF} = 247$ Hz, CF), 126.4 (t, $J_{CF} = 14.4$ Hz, C), 112.3 (t, $J_{CF} = 7.5$ Hz, CH), 111.2 (s, CH), 108.4 (s, C), 98.8 (t, $J_{CF} = 15.1$ Hz, C).

Cp[Fe(η^5-C_5H_4-4,4′-C_6F_4−C_6F_4-η^5-C_5H_4)]$_n$FeCp [3 (n = 1), 4 (n = 2), and 5 (n = 3)]. A solution of NaCp (1.85 g, 21.0 mmol) and dibasic ligand (**2**, 0.50 g, 1.0 mmol) in THF (100 mL) was added by canulla to a stirred orange solution of $FeBr_2$ (1.98 g, 9.7 mmol) in THF (250 mL) at 25 °C. After the addition was complete, the cloudy, dark brown mixture was stirred for an additional 10 min. The solvent was removed under reduced pressure, and the residue was extracted with CH_2Cl_2 (200 mL) and filtered through a 10 cm bed of neutral alumina. The dark red filtrate was evaporated to afford 1.80 g of a red solid. The product mixture was purified by liquid chromatography (50 cm × 5 cm) on silica gel. The first band, eluted with hexanes, was evaporated to afford ferrocene (1.24 g, 6.65 mmol, 69% based on $FeBr_2$). A second band, eluted with 0.5% ethyl acetate in hexanes, was evaporated to afford the diiron complex **3** (0.32 g, 0.49 mmol, 49% based on **2** or 10% based on $FeBr_2$). Data for **3**: ^{1}H NMR ($CDCl_3$): δ 4.90 (pentet, $J_{HH} = J_{HF} = 2.0$ Hz, 4 H), 4.50 (triplet, $J_{HH} = 1.9$ Hz, 4 H), 4.21 (s, 10 H). ^{19}F NMR ($CDCl_3$): δ −141.06 (m, 4 F), −141.24 (m, 4 F). $\{^1H\}^{13}C$ NMR ($CDCl_3$): δ 144.4 (d, $J_{CF} \approx 250$ Hz, two unresolved CF), 121.8 (t, C), 103.7 (m, C), 71.4 (s, C), 70.0 (3 partially resolved singlets, 3 CH). $\{^{19}F\}^{13}C$ NMR ($CDCl_3$): δ 144.4 (s, CF), 144.2 (s, CF), 121.8 (s, C), 103.7 (s, C), 70.0 (complex multiplet). Anal. Calcd for $C_{32}H_{18}F_8Fe_2$: C, 57.66; H, 2.72. Found: C, 57.80; H, 2.60.

A third band, eluted with 5% ethyl acetate in hexanes, similarly afforded 54 mg (0.047 mmol, 9% based on **2** or 1.5% based on $FeBr_2$) of **4**. Data for **4**: ^{1}H NMR ($CDCl_3$): δ 4.96 (m, 4 H), 4.85 (br s, 4 H), 4.53 (t, 1.9 Hz, 4 H), 4.48 (t, 1.9 Hz, 4 H), 4.19 (s, 10 H). ^{19}F NMR ($CDCl_3$): δ −140.7 (br m, 4 F), −140.9 (m, 4 F), −141.2 (br s, 8 F). FAB−HRMS Calcd for $C_{54}H_{26}F_{16}[^{56}Fe]_3$ (M^+): m/z 1145.9827, observed 1145.9797.

The red-orange band remaining on the alumina column was eluted with ethyl acetate and evaporated to afford a red solid (47 mg) containing mostly **4** as determined by ^{1}H NMR. About 20 mg of the latter substance was subjected to liquid chromatography on silica gel (15 × 2 cm), eluting with 25% dichloromethane in hexanes. After a colorless forerun, eight 25 mL orange fractions were collected, evaporated, and analyzed by ^{1}H NMR; fractions 1−3 were combined to afford an additional 9.7 mg of **4**; fractions 5 and 6 were combined to afford 3.4 mg of **5**. Data for **5**: ^{1}H NMR ($CDCl_3$): δ 4.95 (m, 4 H), 4.93 (m, 4 H), 4.83 (m, 4 H), 4.52 (m, 8 H), 4.47 (t, $J = 1.9$ Hz, 4 H), 4.19 (s, 10 H). ^{19}F NMR ($CDCl_3$): δ −140.63 (br m, 8 F), −140.88 (br m, 4 F), −141.05 (br m, 4 F), −141.24 (m, 8 F). FAB−HRMS $C_{76}H_{34}F_{24}[^{56}Fe]_4$ (M^+): m/z 1625.9675, observed 1625.9603.

[CpCo(η^5-C_5H_4-4,4′-C_6F_4−C_6F_4-η^5-C_5H_4)CoCp]$^{2+}$[PF_6^-]$_2$ (6). A solution of NaCp (1.76 g, 20 mmol) and dibasic ligand (**2**, 0.47 g, 1.0 mmol) in THF (100 mL) was added by canulla to a stirred, blue solution of $CoBr_2$ (2.19 g, 10.0 mmol) in THF (200 mL) at 25 °C. After the addition was complete, the cloudy, green mixture was stirred for an additional 15 min. The solvent was evaporated, and the residue was taken up in 100 mL of toluene. Water (100 mL) and then HCl (12 M, 5 mL) were added, and air was bubbled through the mixture for 10 min. The resulting dark mixture was filtered through Celite. The biphasic filtrate was separated, and the organic layer was extracted with water (3 × 50 mL). The combined aqueous extracts were washed with ether (2 × 100 mL), and then 25 mL of saturated aqueous KPF_6 was added with vigorous stirring. The yellow precipitate was collected on a filter, washed with water (2 × 10 mL) and ether (2 × 10 mL), and dried in a vacuum desiccator over anhydrous $CaSO_4$ for 2 days to afford a yellow solid. The solid was subjected to liquid chromatography on alumina (20 cm × 5 cm). Fractions containing cobaltocenium species elute as yellow or sometimes green bands. The first, yellow band was eluted with acetone, evaporated, washed with ether to remove traces of diacetone alcohol, and dried under vacuum to afford 1.05 g of cobaltocenium hexafluorophosphate, which was identified by comparing its ^{1}H and ^{19}F NMR spectra with those of a commercial sample (Aldrich). A second, yellow band was eluted with 1% methanol in acetone and evaporated. The resulting yellow residue was rinsed with ether to remove traces of diacetone alcohol to afford 420 mg of a yellow solid, which was tentatively identified as a 10:1 mixture of **6**/**7**. Data for **6**: ^{1}H NMR (acetone-d_6): δ 6.53 (pentet, $J_{HH} = J_{HF} = 1.9$ Hz, 4 H), 6.25 (t, $J_{HH} = 1.9$ Hz, 4 H) 6.45 (s, 10 H). ^{19}F (acetone-d_6): δ −73.8 (d, $J_{FP} = 715$ Hz, 12 F), −138.4 (m, 4 F), −140.3 (m, 4 F). FAB−HRMS calcd for $C_{32}H_{18}F_8Co_2$: ($M^+ - 2\ PF_6$) 671.9945, observed 671.9927. Data for **7** (tentative): ^{1}H NMR (acetone-d_6): δ 6.64 (m, 4 H), 6.51 (m, 4 H), 6.35 (t, $J = 1.9$ Hz, 4 H), 6.24 (t, 1.9 Hz, 4 H). ^{19}F (acetone-d_6): δ −138.0 (m, 4 F), −139.8 (m, 4 F), −140.2 (m, 4 F); integration data reveal the presence of a fourth signal coincident with the resonance at −138.4 assigned to **6**. In a subsequent experiment, identical in all respects except for the amount of dibasic ligand (**2**) used (0.050 g instead of 0.47 g), the second chromatographic band afforded 65 mg of crude **6**, which was purified of diacetone alcohol by triturating with ether (2 × 1 mL) to afford 44 mg of pure **6**, as determined by ^{1}H and ^{19}F NMR spectroscopy.

Results and Discussion

Ligand Synthesis. The synthesis of 4,4′-bis(cyclopentadienyl)octafluorobiphenyl (Scheme 1) is based on the nucleophilic aromatic substitution approach to perfluoroaryl-substituted cyclopentadienes that we reported earlier.[12] The reaction of decafluorobiphenyl with

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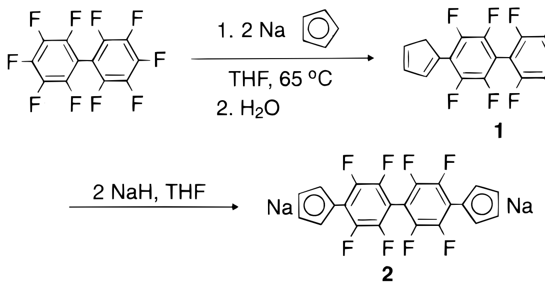
(12) Deck, P. A.; Jackson, W. F.; Fronczek, F. R. *Organometallics* **1996**, *15*, 5287−5291.

Scheme 1



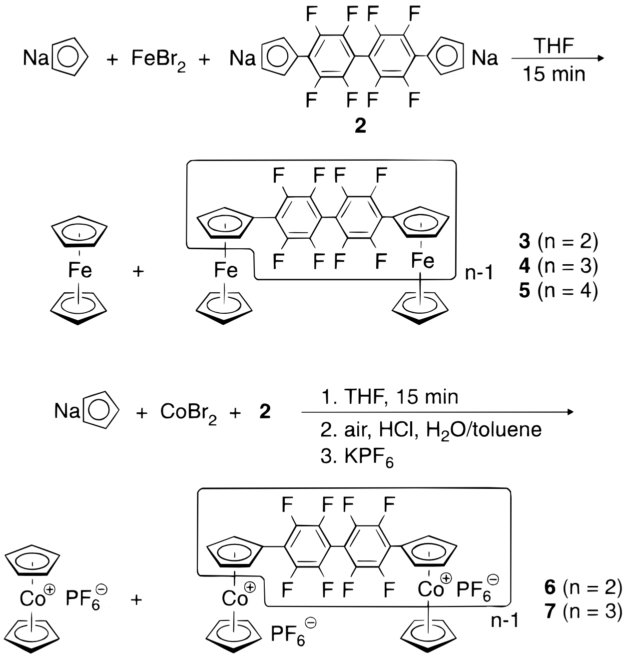
sodium cyclopentadienide and sodium hydride followed by hydrolytic workup results in a nearly quantitative conversion (98% crude, 72% purified) to the bis(cyclopentadiene) (**1**). ^{1}H and ^{19}F NMR spectra obtained for the crude product were consistent with a mixture of double-bond regioisomers and an overall purity of >95%. Initial experiments showed that elevated temperature (65 °C) was needed to ensure alkylation at both the 4 and 4′ positions of the arene. A 10-fold excess of NaCp was used to minimize diarylated cyclopentadiene product. Added sodium hydride was used to trap the product as its conjugate base to prevent intermolecular Diels–Alder dimerization during the arylation reaction; dimers are readily identified by signals in the ^{1}H NMR spectrum characteristic of the tricyclic dicyclopentadiene framework.[12] Treatment of **1** with sodium hydride affords the disodium salt **2** in nearly quantitative yield. The time-averaged D_{2h} symmetry of **2** was confirmed by the presence of only two signals each in the ^{1}H and ^{19}F NMR spectra.

Metallocene Synthesis. Reactions of the dibasic ligand **2** with either $FeBr_2$ or $CoBr_2$ resulted in complex mixtures of step-growth oligometallocenes, which we found difficult to separate and characterize, partly because of the variability and instability of the organic end groups. In subsequent reactions, we therefore used a 21:1:10 ratio of NaCp:**2**:MBr_2. This reactant ratio ensured first that Cp was the predominant end group and second that the product distributions were skewed toward number-average degrees of oligomerization barely exceeding 1.0 metal atoms per molecule. Using this strategy, product mixtures were dominated by Cp_2Fe and $[Cp_2Co]^+[PF_6]^-$ (Scheme 2), from which the minor dimetallic and trimetallic products could be separated.

This strategy worked particularly well for the ferrocene complexes, which are stable and sufficiently soluble in hydrocarbons for separation by gradient liquid chromatography. The diiron, triiron, and tetrairon complexes (**3**, **4**, and **5**, respectively) were isolated and characterized by NMR spectroscopy. The diiron complex was additionally characterized by elemental microanalysis, while the identities of the triiron and tetrairon complexes, which were isolated only in small amounts, were confirmed by high-resolution mass spectrometry.

The ^{1}H NMR spectrum of **3** shows three signals in a 4:4:10 ratio of integrated intensity, whereas the ^{19}F NMR spectrum shows two equally integrating signals. These data are consistent with a time-averaged C_{2h}-symmetric structure in which Cp–C_6F_4 and C_6F_4–C_6F_4 bonds rotate freely. The homologous triiron complex **4** shows the corresponding 10:4:4:4:4 ratio of intensities in the ^{1}H NMR spectrum and the 4:4:4:4 ratio of intensities in the ^{19}F NMR spectrum (two of the signals in the ^{19}F NMR spectrum coincide, giving an observed 4:4:8 ratio.) The tetrairon complex **5** shows the expected 10:4:4:4:4:4:4 ratio in the ^{1}H NMR spectrum (two signals were unresolved, giving an observed 10:4:4:4:4:8 ratio) and the expected 4:4:4:4:4:4 ratio in the ^{19}F NMR (two pairs of signals were unresolved, giving an observed 8:4:4:8 ratio). These data suggest that in **4** and **5** all the Cp–arene bonds also rotate freely.

Scheme 2



The separation and purification of the dicobalt complex were more challenging. The major product, cobaltocenium hexafluorophosphate, was readily separated by liquid chromatography on alumina, eluting with acetone. Unfortunately, we were unable to separate the remaining 10:1 mixture of **6** and **7** by gradient liquid chromatography. Nevertheless, the ^{1}H and ^{19}F NMR spectra of **6** and **7** were analogous to the spectra of **3** and **4**, respectively, and their unambiguous assignment was made possible by resolution-enhancement apodization of the time-domain spectrum (FID) prior to Fourier transformation. A small but pure sample of **6** was obtained in a similar reaction using a 21:0.1:10 ratio of NaCp:**2**:$CoBr_2$ to avoid contamination by the tricobalt species (**7**).

Electrochemical Studies. Solution voltammetry was used to investigate the possibility of "electronic communication" between the two metal centers in the homobimetallic complexes (**3** and **6**).[3f,13] The results of these analyses are presented in Table 2. Significant metal–metal interaction would be indicated by two distinct oxidation waves in either cyclic voltammetry (CV) or Osteryoung square wave voltammetry (OSWV). However, when the diiron complex (**3**) was subjected to these two measurements, only one oxidation wave was observed. In fact, the fwhm of the OSWV signal of **3** was the same as that of internal ferrocene. This means that the two ferrocenyl groups oxidize independently

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and that no communication between the two Fe centers was observed. An analogous biphenylene-linked diferrocene species of the formula (η^5-C_5Me_5)Fe(η^5-C_5Me_4)-C_6H_4–C_6H_4-(η^5-C_5Me_4)Fe(η^5-C_5Me_5) also showed no voltammetric splitting;[14] however one might expect the conjugation between the cyclopentadienyl and aryl groups to be disrupted by the presence of the additional methyl groups on the Cp ligands (which facilitated the synthesis of the complex).[15] Interestingly, the increase in the $Fe^{II}|Fe^{III}$ oxidation potential relative to internal ferrocene of +200(5) mV observed for **3** is slightly larger than the effect anticipated for a single pentafluorophenyl substituent of +173(5) mV.[12] This demonstrates the ability of the 4,4′-octafluorobiphenylene unit to render *both* coordinated transition-metal fragments highly electron-deficient simultaneously.

Similar observations were made when the dicobalt complex (**6**) was subjected to solution voltammetry. A single, reversible wave was observed in the cyclic and Osteryoung square wave voltammograms of **6**, suggesting that no significant communication between the two equivalent Co^{III} centers exists. A reduction potential of +232(5) mV relative to internal Cp_2Co^+ is slightly higher than that expected for a single C_6F_5 substituent of +200(5) mV,[16] again showing that the bridging ligand (**2**) renders both Co^+ centers electron-poor.

CV analysis of **4** showed two reversible oxidations in an approximately 2:1 current ratio. Analysis by OSWV showed two peaks at +180(5) and +372(5) mV, respectively, relative to internal ferrocene. The center ferrocene unit is substituted by two perfluoroarylene groups, whereas the terminal ferrocene units are substituted by only one, leading to the observed oxidation potentials in accord with the substituent effects described for the diiron complex (**3**). The observation that no significant *additional* potential is required to oxidize the center metallocene unit beyond that predicted on the basis of substituent effects also demonstrates the independence of the ferrocene units of **4**. The tetrairon complex (**5**) showed similar voltammetric behavior: CV analysis showed two reversible oxidation waves, which were found by subsequent OSWV analysis to have a 2:2 current ratio at +192(5) and +382(5) mV versus internal ferrocene.

X-ray Crystal Structure of 3. Table 1 shows the crystal data for the diiron complex (**3**). Figure 1 shows a thermal ellipsoid plot of the solid-state structure of **3**, defines an atom-numbering scheme, and provides selected metric data. All four Cp rings exhibit highly regular pentahapto coordination with all Fe–C distances within a narrow range (2.028–2.054 Å). The unsubstituted Cp ligands are only slightly farther (0.01 Å, measured from the C_5 centroids) from the respective iron atoms than the substituted Cp ligands.[17] The torsion angles between least-squares planes of the dibasic ligand are Cp-37.5°-C_6F_4-50.1°-C_6F_4-32.1°-Cp. These conformational preferences had been anticipated from the torsion angle of decafluorobiphenyl (70° in the gas phase[18] and 64.4° in the solid state[19]) and from the Cp–C_6F_5 torsion angles (25–45°) in other C_6F_5-substituted ferrocenes that we have studied.[20]

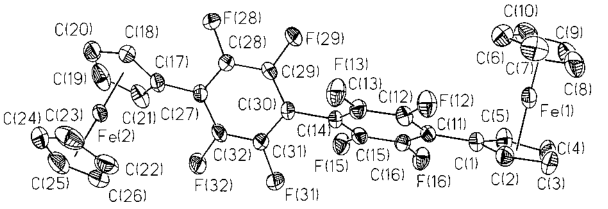

Figure 1. Thermal ellipsoid plot of **3** (50% probability) showing atom-labeling scheme. Hydrogen atoms were located and isotropically refined but are omitted from this view. Selected bond distances (Å) and angles (deg): Cent$_{C(1)-C(5)}$–Fe(1), 1.650(4); Cent$_{C(6)-C(10)}$–Fe(1), 1.657(4); Cent$_{C(17)-C(21)}$–Fe(2), 1.647(4); Cent$_{C(22)-C(26)}$–Fe(2), 1.656; Cent$_{C(1)-C(5)}$–Fe(1)–Cent$_{C(6)-C(10)}$, 178.2(2); Cent$_{C(17)-C(21)}$–Fe(2)–Cent$_{C(22)-C(26)}$, 178.3(2); Cent$_{C(1)-C(5)}$–C(1)–C(11), 177.2(2); Cent$_{C(17)-C(21)}$–C(17)-C(27), 177.1(2); C(1)–C(11), 1.474(4); C(17)–C(27), 1.476(4); C(14)–C(30), 1.501(4); C(12)–C(11)–C(16), 114.6(3); C(13)–C(14)–C(15), 115.7(3); C(29)–C(30)–C(31), 116.0(3); C(28)–C(27)–C(32), 114.4(3).

Conclusions

Nucleophilic aromatic substitution is an efficient route to dibasic bis-Cp ligands tethered by the 4,4-octafluorobiphenylene spacer. This highly fluorinated spacer exerts a strong electron-withdrawing influence on both coordinated CpFe fragments in **3**. However, despite the conjugated nature of the spacer, no electronic "communication" between the two CpFe fragments was evident from voltammetric analysis. We are continuing to investigate the synthesis and characterization of homo- and heterobimetallic cyclopentadienyl complexes linked by perfluoroarylene spacers.

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Supporting Information Available: Crystallographic data for the diiron complex **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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