collected with graphite-monochromatized Mo K$\alpha$ radiation, using the $\theta/2\theta$ scan technique. No intensity decay was observed during the data collection period. Lorentz–polarization and absorption corrections were made (maximum and minimum transmission factors are 0.86 and 0.80, respectively). Details are given in Table II.

The structure was solved by direct methods, using the MULTAN system of computer programs,[21] which gave the position of the 20 heaviest atoms. The remaining non-hydrogen atoms were obtained from a subsequent weighted Fourier synthesis. The structure was refined by a full-matrix least-squares method using the Shelx 76 computer program.[22] The function minimized was $w(|F_o| - |F_c|)^2$, where $w = \sigma^{-2}|F_o|$. As the number of observed reflections was limited by the poor quality of the crystal, each phenyl ring was refined with constrained geometry (planar, C–C = 1.395 Å, and C–C–C = 120°) and with overall anisotropic thermal coefficients, in order to reduce the number of parameters to be refined. A difference synthesis showed a disorder in the localization of the C(11), C(14), and C(15) atoms of the cyclopentadienyl and the C(23)O(23) ligand, which were refined with an occupancy factor of 0.5, according to peaks observed in a Fourier synthesis. The refinements results are given in Table II.

The final positional parameters of the refined atoms are given in Table IV. A table of thermal parameters, a full list of bond distances and angles, and a table of observed and calculated structure factor amplitudes are available as supplementary material.[23]

**Acknowledgment.** This work has been partly supported by a grant from the CSIC and by the CNRS. P.B. is grateful to Drs. B. Metz and B. Chevrier for drawings of **2** obtained in the Laboratoire de Cristallographie Biologique, IBMC du CNRS, Strasbourg, France.

**Registry No.** **1**, 101224-88-8; **2**, 101224-89-9; $Pt(C_2H_4)(PPh_3)_2$, 12120-15-9; $(C_6Cl_5)Hg–M_0(CO)_3C_p$ 93939-29-8; $(C_6Cl_5)Hg–W(CO)_3Cp$, 93939-32-3.

**Supplementary Material Available:** Complete lists of bond lengths and angles (Table SI), thermal parameters (Table SII), and observed and calculated structure factors (Table SIII) for **2** and a view of the molecular structure of **2** with the complete numbering scheme (Figure 2) (16 pages). Ordering information is given on any current masthead page.

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[23] See paragraph at end of paper regarding supplementary material.

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# Synthesis, Molecular Structure, and 2-D NMR Analysis of Bis(tetraphenylcyclopentadienyl)iron(II)

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Tetraphenylcyclopentadiene (I) may be prepared in 82% yield in a one-step synthesis from tetraphenylcyclopentadienone. The reaction between $Li(C_5HPh_4)$ (II) and $FeCl_2$ in THF solvent produces $(C_5HPh_4)_2Fe$ (III). Treatment of the latter complex with $AgPF_6$ affords $[(C_5HPh_4)_2Fe]PF_6$. The oxidation potential of III is similar to that of ferrocene. Crystals of III belong to the space group $P\bar{1}$ with $a = 8.339$ (4) Å, $b = 10.867$ (5) Å, $c = 12.830$ (7) Å, $\alpha = 66.40$ (4)°, $\beta = 73.471$ (4)°, $\gamma = 83.721$ (4)°, and $V = 1021.3$ (9) Å$^3$. Solution of the structure led to final values of $R = 4.52$ and $R_w = 5.09$. Complex III possesses rigorous inversion symmetry in the solid state and the two cyclopentadienyl rings adopt a staggered 180° configuration. Phenyl-substituted carbon–iron distances (average Fe–C = 2.094 (3) Å) are significantly longer than for the methine carbon (Fe–C = 2.054 (3) Å) of the cyclopentadienyl ring and longer than similar Fe–C distances in $(C_5H_5)_2Fe$, $(C_5Me_5)_2Fe$, and $(C_5HMe_4)_2Fe$. Through a combination of $^1H$ COSY NMR spectroscopy, selective deuteration of III, and $^{13}C$ NMR spectroscopy, with selective proton decoupling, a complete assignment of proton and carbon NMR spectra is provided. Analysis of the temperature dependence of the 500-MHz $^1H$ NMR spectra suggests that rotation of the two tetraphenylcyclopentadienyl rings is rapid to −95 °C; however, ordering of the phenyl ring conformations occurs below −20 °C. Spectral data suggest that at low temperature the phenyl rings adjacent to the lone cyclopentadienyl hydrogen become coplanar with the $C_5$ ring and the remaining phenyl groups lie perpendicular to this plane.

## Introduction

The cyclopentadienyl ligand has occupied a central role in the development of organometallic chemistry.[2] Methyl-substituted derivatives, especially pentamethylcyclopentadienyl,[3] have been used in place of cyclopentadienyl because of their increased steric bulk, solubility, stability, and electron donor properties. Coordination chemistry of other cyclopentadienyl ligands that can be prepared conveniently has not been developed extensively. A few complexes that contain the pentaphenylcyclopentadienyl ligand are known;[4-8] however, this ligand limits access to

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[1] (a) University of California at San Diego. (b) University of Delaware.

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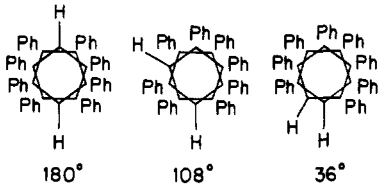
the metal center, solubilities are low, and the ligand synthesis requires several steps. An alternative hindered arylcyclopentadiene would be tetraphenylcyclopentadiene. The lower symmetry of the ligand might enhance solubilities of complexes. It can also be prepared in one step (82% yield) from commercially available tetraphenylcyclopentadienone. For bis(tetraphenylcyclopentadienyl) metal complexes there are interesting questions about the stability of rotamers of the two cyclopentadienyl rings and about phenyl ring orientations. Three possible arrangements of the cyclopentadienyl rings are



Tetraphenylcyclopentadienyl metal complexes have not yet been structurally characterized. The design of substrate specific homogeneous catalysts[9] requires an understanding of ligand conformational properties so that ligand-binding pockets can be tailored to fit specific substrates. Herein we report an efficient synthesis of $(C_5HPh_4)_2Fe$ and its solid state and solution structures as well as its redox properties.

## Experimental Section

All reactions of moisture-sensitive materials were performed under a nitrogen atmosphere employing standard Schlenk techniques. Solids were manipulated under nitrogen in a Vacuum Atmospheres glovebox equipped with a HE-493 dri-train. Diethyl ether and THF were refluxed over sodium–benzophenone ketyl and distilled under nitrogen. Methylene chloride was refluxed over $CaH_2$ and distilled under nitrogen. Other solvents were used without purification. All reagents, except $FeCl_2$ (Alfa), tetraphenylcyclopentadienone (Eastman-Kodak and Aldrich) and 1,3-diphenyl-2-propanone (Lancaster Synthesis) were purchased from Aldrich Chemical Co. and used without purification.

Optical spectra were obtained with an IBM 9420 UV-vis spectrophotometer. Cyclic voltammograms were recorded with an IBM EC/225 polarographic/voltammetric analyzer and a 7422MT x-y-t recorder. A conventional three-electrode cell (Pt button working electrode, Pt wire auxiliary electrode, and a $Ag/Ag^+$ (0.1 M $AgNO_3$ in $CH_3CN$) reference electrode) was employed. Tetra-*n*-butylammonium perchlorate (Baker electrochemical grade) was used as the backing electrolyte. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories.

**NMR Spectroscopy.** Most $^1H$ NMR spectra were recorded at 360.247 MHz with a spectrometer built[10] at the UCSD Chemistry Department NMR facility. Some variable-temperature studies were recorded at 500.132 MHz with a Bruker WM-500 located at the Southern California Regional NMR Facility at the California Institute of Technology. The $^{13}C$ NMR spectra were obtained with a Nicolet 200 instrument at 50.31 MHz.

A $^1H$ COSY (correlated spectroscopy) spectrum was obtained at 360.242 MHz, using a 16-step phase cycle to suppress axial peaks and artifacts from quadrature imbalance and to provide phase modulation in $t_2$. The spectral window of ±100 Hz was centered at $\delta$ 6.95. Resonances outside this window, from traces of water, undeuterated solvent, and the cyclopentadienyl ring protons, were suppressed by a 100-Hz four-pole Butterworth filter. A 90° pulse (6.5 $\mu$s) was used for both $P_1$ and $P_2$. Thirty-two 512 point FID's (acquisition time of 1.28 s) were accumulated at each of 256 $t_1$ values (5-ms increment). The resulting symmetrical data matrix was treated by multiplying by a sine bell and zero-filling before Fourier transformation in each dimension. The data matrix was magnitude calculated after the second FT; it was not symmetrized.

**Synthesis of Tetraphenylcyclopentadiene (I).** This compound was prepared by modifying a literature method,[11] which increased the yield by nearly twofold. To a 1-L 3-neck flask equipped with a condenser and mechanical stirrer was added 500 g of anhydrous diethyl ether and 25.0 g (65.0 mmol)of tetraphenylcyclopentadienone ($Ph_4C_5O$). While the solution was stirred in an ice bath, 18.0 g (135 mmol) of $AlCl_3$ followed by 5.00 g (132 mmol) of $LiAlH_4$ were added slowly in air (use of rigorously anhydrous conditions results in no reaction). During addition of the $LiAlH_4$ the mixture turned from deep purple to yellow-green. The ice bath was replaced with a heating mantle, and the mixture was refluxed for 18–24 h under a nitrogen atmosphere to produce a gray mixture. Heating was discontinued, and dilute hydrochloric acid was used to quench excess hydride reagent. The ether layer was decanted from the aqueous phase, and the heterogeneous aqueous layer was extracted with benzene until no visible product remained. The benzene and ether fractions were combined, washed with saturated $NaHCO_3$ (3 times) and then water (3 times), and dried over $CaCl_2$. Solvent was removed yielding 23.5 g (63.3 mmol, 97%) of I. Recrystallization from boiling heptane yields I (mp 180–181 °C (lit.[12] 180–182 °C)) as yellow crystals in 82% net yield.

**Synthesis of Lithium Tetraphenylcyclopentadienide (II).** To a stirred solution of 10.0 g (27.0 mmol) of I in benzene was added 18.0 mL of 1.55 M *n*-BuLi (28.6 mmol) in hexanes. After 1 h a white precipitate formed and congealed into a paste.[13] Solvents were removed under dynamic vacuum, and the solid product was ground to a powder under nitrogen with a mortar and pestle.

**Synthesis of Bis(tetraphenylcyclopentadienyl)iron(II) (III).** Dry THF (10 mL) was added to a solid mixture of anhydrous $FeCl_2$ (0.10 g, 0.79 mmol) and II (0.62 g, 1.65 mmol). After the mixture was stirred overnight, the THF was removed, and the resulting solid was added to 80 mL of toluene and heated to boiling in the air. The hot solution was filtered rapidly and reheated to boiling. After the volume was reduced, the flask was cooled to −15 °C overnight. Red, air-stable, crystalline III was isolated in 58% yield (0.36 g). Anal. Calcd for $C_{58}H_{42}Fe$: C, 87.65; H, 5.33. Found: C, 87.45; H, 5.49. UV-vis: $\lambda_{max}$ ($CH_2Cl_2$) 502 nm ($\epsilon$ 520), 340 (14000), 262 (52000).

**Synthesis of Bis(tetraphenylcyclopentadienyl)iron(III) Hexafluorophosphate (IV).** To a mixture of III (0.35 g, 0.44 mmol) and $AgPF_6$ (0.13 g, 0.51 mmol) was added 15 mL of $CH_2Cl_2$. A deep red solution formed immediately. After being stirred overnight, the solution was cannula filtered into a Schlenk tube containing an empty test tube. The residue was extracted with $CH_2Cl_2$ until all product had been removed. The empty test tube was filled with diethyl ether, the pressure was reduced, and the Schlenk tube was cooled to −15 °C. After 5 days the solution was cannula filtered and the test tube was removed. Black needles of IV (0.32 g, 78%) were dried in vacuo. Anal. Calcd for $C_{58}H_{42}F_6FeP$: C, 74.13; H, 4.50. Found: C, 74.05; H, 4.80. UV-vis: $\lambda_{max}$ ($CH_2Cl_2$) 750 nm ($\epsilon$ 165), 495 (5040), 372 (15000), 248 (45000).

**Synthesis of Bis(2,3-diphenyl-$d_{10}$-1,4-diphenylcyclopentadienyl)iron(II) (V).** Benzaldehyde-$d_5$,[14] benzoin-$d_{10}$,[15] and benzil-$d_{10}$[16] were successively prepared by literature syntheses from

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**Table I. Crystal and Refinement Data for Octaphenylferrocene**

| | |
|---|---|
| formula | $C_{58}H_{42}Fe$ |
| cryst system | triclinic |
| space group | $P\bar{1}$ |
| $a$, Å | 8.339 (4) |
| $b$, Å | 10.867 (5) |
| $c$, Å | 12.830 (7) |
| $\alpha$, deg | 66.40 (4) |
| $\beta$, deg | 73.471 (4) |
| $\gamma$, deg | 83.721 (4) |
| $V$, Å$^3$ | 1021.3 (9) |
| $Z$ | 1 |
| temp, °C | 24 |
| cryst dimens, mm | 0.31 × 0.31 × 0.31 |
| radiation | graphite-monochromated Mo K$\alpha$ ($\lambda$ = 0.71073 Å) |
| $D$(calcd), g cm$^{-3}$ | 1.292 |
| diffractometer | Nicolet R3 |
| abs coeff, cm$^{-1}$ | 4.2 |
| scan speed, deg/min | variable 5–20 |
| $2\theta$ scan range, deg | 4–52 |
| scan technique | omega |
| data collected | $\pm h, \pm k, +l$ |
| weighting factor, $g$ | 0.000 80 [$w^{-1} = \sigma^2(F_o) + gF_o^2$] |
| unique data | 4019 (4209 collected) |
| unique data, $(F_o) > 3\sigma(F_o)$ | 3498 |
| std rflns | 3 stds/197 rflns |
| no. of refinement parameters | 225 |
| GOF | 1.432 |
| $R_F$, % | 4.52 |
| $R_{wF}$, % | 5.09 |

benzene-$d_6$. Benzil-$d_{10}$ was condensed with 1,3-diphenyl-2-propanone to yield 3,4-diphenyl-$d_{10}$-2,5-diphenylcyclopentadienone,[17] which was converted to V according to procedures detailed above for III.

**X-ray Diffraction Study of Bis(tetraphenylcyclopentadienyl)iron(II) (III).** A well-formed crystal was grown for X-ray analysis by vapor diffusion of pentane into a saturated $CH_2Cl_2$ solution of III. Crystal data and parameters used during the collection of intensity data are given in Table I. A deep red crystal was attached to a fine glass fiber with epoxy cement. The compound was found to crystallize in the triclinic space group $P\bar{1}$. Unit-cell dimensions were derived from a least-squares fit of the angular settings of 25 reflections with 20° < $2\theta$ < 30°. A profile fitting procedure was applied to all intensity data to improve the precision of the measurement of weak reflections.

The structure was solved intuitively, locating the Fe atom at the origin. The remaining non-hydrogen atoms were located from subsequent difference Fourier syntheses. All non-hydrogen atoms were refined anisotropically employing idealized, isotropic hydrogen atom contributions ($d$(C–H) = 0.96 Å, $U$ = 1.2$U$ of attached C) for all hydrogen atoms except H(1), which was located and refined. Phenyl rings were treated as rigid hexagons, $d$(C–C) = 1.395 Å. An absorption correction was not needed because of uniform crystal dimensions and the low absorption coefficient (4.2 cm$^{-1}$). The final difference Fourier synthesis showed only a diffuse background (maximum contour 0.35 e/Å$^3$). An inspection of $F_o$ vs. $F_c$ values and trends based on sin $\theta$, Miller index, or parity group did not show systematic errors in the data. All computer programs used in the data collection and refinement are contained in the Nicolet program packages P3, SHELXTL (version 4.10), and XP.

The Fe atom of octaphenylferrocene resides at a crystallographic center of symmetry. Atomic coordinates are provided in Table II, selected bond distances in Table III, and least-squares planar calculations in Table IV. Additional data are available as supplementary material.

## Results and Discussion

**Synthesis.** Several syntheses of tetraphenylcyclopentadiene have been reported;[11,12,18-21] however, only more

**Table II. Atomic Coordinates (×10$^4$) and Isotropic Thermal Parameters (Å$^2$ × 10$^3$) for Octaphenylferrocene**

| | $x$ | $y$ | $z$ | $U^a$ |
|---|---|---|---|---|
| Fe | 0 | 0 | 0 | 33(1) |
| C(1) | 2034 (3) | 1148 (3) | −348 (2) | 38(1) |
| C(2) | 2133 (3) | 871 (3) | −1358 (2) | 38(1) |
| C(3) | −2191 (3) | 564 (3) | 993 (2) | 37(1) |
| C(4) | −2152 (3) | 1137 (3) | −230 (2) | 39(1) |
| C(5) | 2083 (3) | −71 (3) | 632 (2) | 38(1) |
| C(21) | 3101 (2) | 3114 (2) | −2865 (2) | 53(1) |
| C(22) | 3216 | 4143 | −3970 | 71(2) |
| C(23) | 2522 | 3971 | −4773 | 77(2) |
| C(24) | 1712 | 2771 | −4470 | 63(2) |
| C(25) | 1597 | 1742 | −3364 | 46(1) |
| C(26) | 2291 | 1913 | −2562 | 41(1) |
| C(31) | −1688 (2) | 2535 (2) | 1412 (2) | 54(1) |
| C(32) | −2099 | 3274 | 2124 | 75(2) |
| C(33) | −3359 | 2819 | 3178 | 83(2) |
| C(34) | −4209 | 1625 | 3519 | 75(2) |
| C(35) | −3798 | 887 | 2807 | 55(1) |
| C(36) | −2537 | 1342 | 1753 | 43(1) |
| C(41) | −1308 (2) | 3534 (2) | −1657 (2) | 58(1) |
| C(42) | −1750 | 4874 | −2173 | 71(2) |
| C(43) | −3406 | 5269 | −1866 | 74(2) |
| C(44) | −4621 | 4324 | −1042 | 73(2) |
| C(45) | −4179 | 2984 | −526 | 55(1) |
| C(46) | −2522 | 2589 | −833 | 42(1) |
| C(51) | 1686 (3) | 953 (2) | 2108 (2) | 51(1) |
| C(52) | 1641 | 877 | 3228 | 64(2) |
| C(53) | 2069 | −316 | 4055 | 66(2) |
| C(54) | 2542 | −1432 | 3761 | 67(2) |
| C(55) | 2588 | −1355 | 2641 | 58(1) |
| C(56) | 2160 | −163 | 1815 | 43(1) |

[a] Equivalent isotropic $U$ defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

**Table III. Selected Bond Distances (Å) for Octaphenylferrocene**

| | | | |
|---|---|---|---|
| Fe–CNT | 1.695 (2) | C(46)–C(4) | 1.496 (3) |
| C(1)–C(2) | 1.423 (5) | C(56)–C(5) | 1.500 (4) |
| C(2)–C(3) | 1.438 (4) | C(1)–H(1) | 1.003 (31) |
| C(3)–C(4) | 1.429 (4) | Fe–C(1) | 2.054 (3) |
| C(4)–C(5) | 1.435 (5) | Fe–C(2) | 2.093 (2) |
| C(5)–C(1) | 1.421 (3) | Fe–C(3) | 2.097 (2) |
| C(26)–C(2) | 1.483 (3) | Fe–C(4) | 2.088 (3) |
| C(36)–C(3) | 1.481 (4) | Fe–C(5) | 2.099 (3) |

**Table IV. Least-Squares Planes for Octaphenylferrocene**

Plane I: $0.9987X + 0.0351Y + 0.0358Z - 1.6952 = 0$

| atoms | dev | atoms | dev |
|---|---|---|---|
| C(1) | −0.0119 | C(4) | −0.0059 |
| C(2) | −0.0081 | C(5) | 0.0109 |
| C(3) | −0.0013 | CNT$^a$ | −0.0004 |

Plane II: $0.8647X - 0.3801Y - 0.3283Z - 1.4911 = 0$

Plane III: $0.6757X - 0.5141Y + 0.5284Z - 0.8852 = 0$

Plane IV: $0.1818X + 0.1807Y + 0.9666Z - 0.4209 = 0$

Plane V: $0.9541X + 0.2967Y + 0.0412Z - 1.7111 = 0$

| plane | atoms |
|---|---|
| I | C(1), C(2), C(3), C(4), C(5) |
| II | C(21), C(22), C(23), C(24), C(25), C(26) |
| III | C(31), C(32), C(33), C(34), C(35), C(36) |
| IV | C(41), C(42), C(43), C(44), C(45), C(46) |
| V | C(51), C(52), C(53), C(54), C(55), C(56) |

Dihedral Angles Between Planes

| | II | III | IV | V |
|---|---|---|---|---|
| I | 33.0 | 47.5 | 77.1 | 15.3 |
| II | | 52.7 | 103.2 | 45.7 |
| III | | | 57.3 | 59.1 |
| IV | | | | 74.5 |

[a] Not used in plane calculation.

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**Table V. Electrochemical Data for Ferrocene Derivatives**

| compd | $E_{1/2}$[a] | $\sigma_{meta}$[b] | $\sigma_{para}$[b] |
|---|---|---|---|
| $Cp_2Fe$ | 0.07 | H, 0.00 | 0.00 |
| III | 0.10 | Ph, 0.06 | -0.01 |
| $(C_5Me_5)_2Fe$ | -0.48 | Me, -0.07 | -0.17 |

[a] In V, vs. $Ag/Ag^+$ in $CH_2Cl_2$ solution with 0.1 M TBAP as backing electrolyte. [b] Reference 24.

recent preparations[11,20,21] have claimed good yields and convenient procedures. Although the synthesis of I via Wolff-Kischner reduction was reported[20] to occur in 80% yield, the reaction does not work well in our laboratory. The procedure of Cava and Narasimhan[11] (eq 1) was

$$C_5Ph_4(O) + LiAlH_4 + AlCl_3 \xrightarrow[\Delta]{Et_2O} I \qquad (1)$$

modified (see Experimental Section), which led to an increase in yield from 48 to 82%. Compound I deprotonates with *n*-butyllithium to yield $Li[C_5HPh_4]$, which is isolated as a white powder. Syntheses of octaphenylferrocene (III) have been reported by Weinmayr[22] and by McVey and Pauson.[7] These early preparations proceeded in low yields[7] and used inconvenient reaction conditions.[7,22] Pauson found that the straightforward synthesis (eq 2) failed to

$$FeCl_2 + 2Li(C_5HPh_4) \rightarrow (C_5HPh_4)_2Fe \qquad (2)$$

yield III when diethyl ether was chosen as reaction solvent.[23] With THF as solvent, both reactants have substantially higher solubility and we have obtained III in 58% yield according to eq 2. Complex III forms brick-red crystals with moderate solubility in benzene, $CH_2Cl_2$, and THF. Treatment of III with $AgPF_6$ in $CH_2Cl_2$ solvent yields $[III][PF_6]$ in analytically pure form.

Cyclic voltammograms of III, $Cp_2Fe$, and $(C_5Me_5)_2Fe$ were obtained in methylene chloride solution with 0.1 M tetra-*n*-butylammonium perchlorate (TBAP) as backing electrolyte. All complexes exhibit reversible one-electron oxidations. From the data compiled in Table V it can be seen that the $E_{1/2}$ values for these complexes vary according to

$$E_{1/2}(C_5HPh_4)_2Fe \simeq E_{1/2}(Cp_2Fe) \gg E_{1/2}(C_5Me_5)_2Fe$$

These electrochemical data agree with the inductive effects of the substituents as ordered by Hammett coefficients (Table V).[24] Hammett coefficients for phenyl substituents are close to those for hydrogen, while those for methyl groups are larger and more negative. When a solution of III in THF with 0.25 M TBAP supporting electrolyte was swept to -2.6 V (vs. $Ag/Ag^+$), reduction was not observed.

**Structure.** The structure of III (Figure 1) is the first of a compound containing tetraphenylcyclopentadiene as a ligand.[25] Compound III crystallizes as discrete well-separated molecules with a staggered $C_5$ ring configuration on a crystallographic center of symmetry (Figure 2). Thus, in the solid state the 180° rotamer, expected to be most stable from steric considerations, is observed. In III the Fe-(ring C) bond distances of phenyl-substituted carbons (average 2.094 (3) Å) exceed the iron-carbon bond distance for the unsubstituted carbon (2.054 (3) Å). Iron-carbon bond distances to the phenyl-substituted carbons are significantly longer than similar distances in $Cp_2Fe$ (2.045 Å),[26] $(C_5HMe_4)_2Fe$ (2.054 (3) Å),[27] and $(C_5Me_5)_2Fe$ (2.050 (2) Å).[28] Unlike III, all the Fe-(ring C) bond lengths are the same in $(C_5HMe_4)_2Fe$. The (ring C)-(ring C) distances for the family of metallocenes III, $Cp_2Fe$, $(C_5HMe_4)_2Fe$, and $(C_5Me_5)_2Fe$ are similar (1.429 (2), 1.40 (2), 1.428 (3), 1.419 (2) Å).

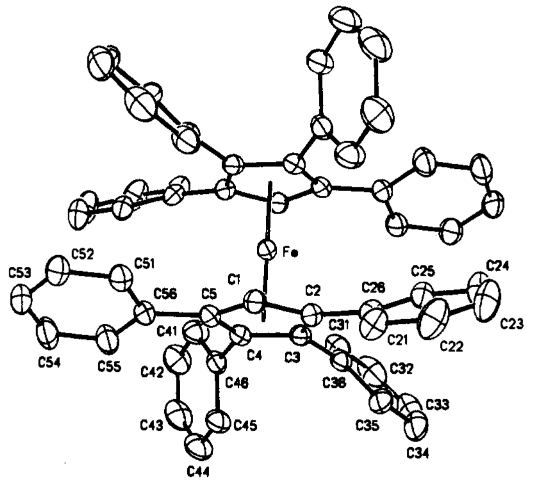

**Figure 1.** Thermal ellipsoid diagram and labeling scheme for octaphenylferrocene. The Fe atom occupies a crystallographic center of symmetry.

**Table VI. Cyclopentadienyl and Phenyl Dihedral Angles of I and III**

| Cp carbon | III[a] | I[a,b] |
|---|---|---|
| 2 | 33.0 | 32.5 |
| 3 | 47.5 | 69.0 |
| 4 | 77.1 | -69.2 |
| 5 | 15.3 | -22.8 |

[a] In degrees. [b] Reference 29.

In free tetraphenylcyclopentadiene[29] the (ring C)-(ring C) distances vary because the system is not aromatic. The (ring C)-(phenyl C) distances do not vary either within the molecules or between them (I, 1.471 (7) Å; III, 1.490 (4) Å). One difference between I and III is in the dihedral angles the phenyl groups make with the cyclopentadienyl plane. While the absolute values of the dihedral angles are similar (Table VI), the directions the phenyl rings tilt is not. Phenyl rings in III cant in the same direction (Figure 3), whereas in I the rings tilt in the direction of the unsubstituted carbon.

**Solution Structure of III.** Because of low steric hindrance, cyclopentadienyl ring rotation barriers have been measured for only two ferrocene derivatives.[30,31] The presence of eight phenyl substituents in III suggested that this barrier might be seen by variable-temperature NMR spectroscopy. Assignment of the $^1H$ NMR spectrum (Figure 4) was first necessary.

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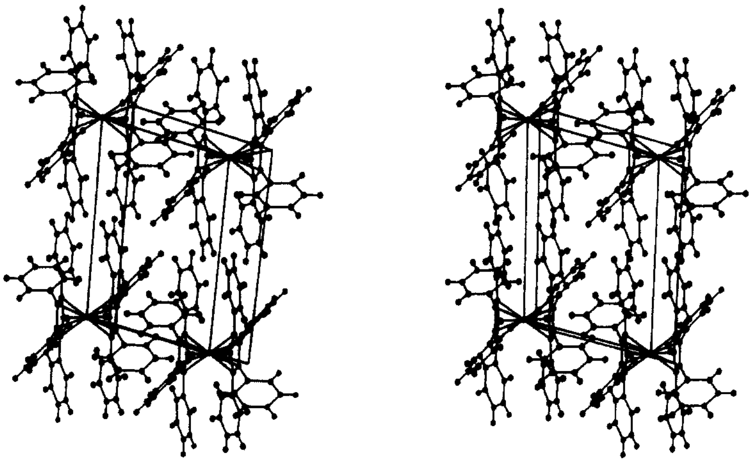

**Figure 2.** Stereoview of the unit cell packing for octaphenylferrocene as viewed down the *b* axis.

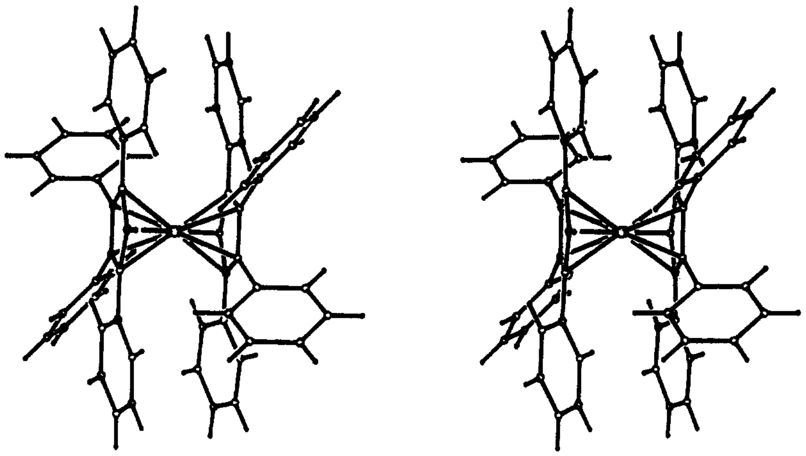

**Figure 3.** Molecular stereoview for octaphenylferrocene.

**Table VII. Assignment of the $^1$H COSY[a] NMR Spectrum of $(C_5HPh_4)_2Fe$**

| pattern location[a,b] Row, | Column | pattern type | interpretation |
|---|---|---|---|
| (1,2) | (2,1) | 2 × 3 | a coupled to b, but not to x |
| (1,3) | (3,1) | 2 × 3 | a coupled to c or y |
| (1,4) | (4,1) | none | a not coupled to z |
| (2,2) | | 2 × 2, 3 × 3 | x not coupled to b |
| (2,3) | (3,2) | 2 × 3, 2 × 3 | b and x coupled to c and y |
| (2,4) | (4,2) | 3 × 2 | x coupled to z |
| (3,4) | (4,3) | 3 × 3 | c or y coupled to z |

[a] Bax, A. *Two-Dimensional Nuclear Magnetic Resonance in Liquids*; D. Reidel: Boston, 1982. [b] COSY gives a symmetrical two-dimensional plot with the normal spectrum appearing along the principal diagonal. Off-diagonal peaks at frequencies $f_1$, $f_2$ arise from scalar coupling between resonances at $f_1$ and $f_2$ in the normal spectrum.

The room-temperature $^1$H NMR spectrum of III in THF-$d_8$ (Figure 4) consists of four multiplets. From low field, there appear to be a doublet, a, a four-peak multiplet, and two triplets, with relative areas of 2:3:3:2. The four-peak multiplet appears to consist of an overlapping triplet, b, and a doublet, x. The integration and $^1$H COSY spectrum (Figure 4) support this assignment and further show that one apparent triplet consists of superimposed triplets c and y. Consideration of the $^1$H COSY spectrum of III (Table VII) shows that multiplets a, b, and c are coupled to each other, as are x, y, and z. A model consistent with these data is one in which all phenyl groups rotate rapidly on the NMR time scale. On the basis of the couplings and integrated intensities, doublets a and x can be assigned to ortho protons, triplets b and y to para protons, and triplets

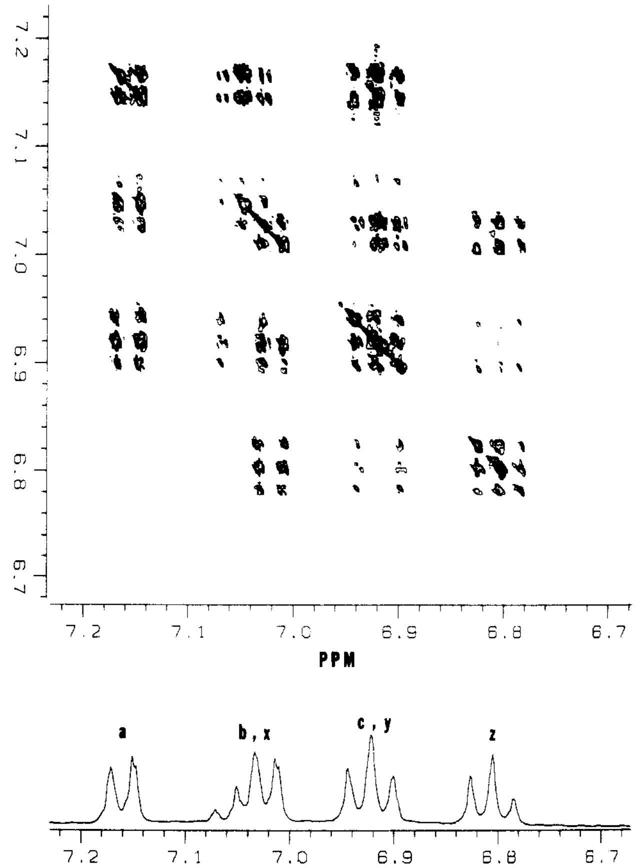

**Figure 4.** 2-D COSY $^1$H NMR spectrum of octaphenylferrocene in THF-$d_8$ solvent.

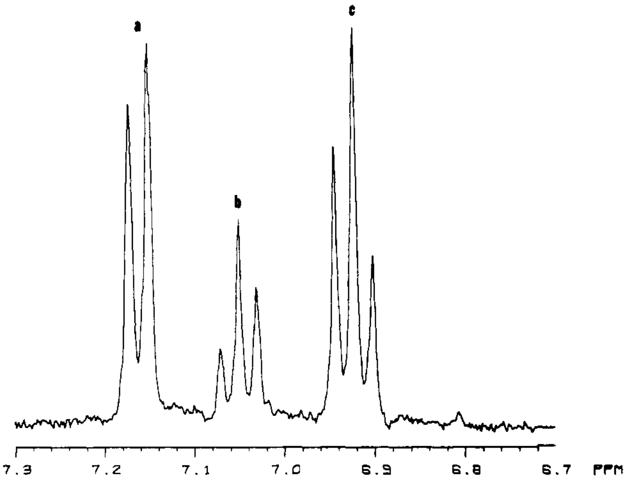

**Figure 5.** $^1H$ NMR spectrum of octaphenylferrocene, with phenyl rings 3 and 4 deuterated, in THF-$d_8$ solvent.

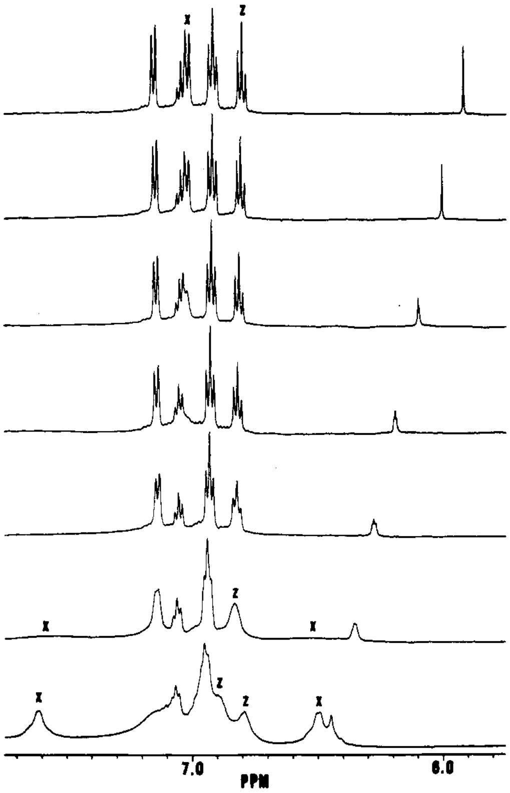

**Figure 6.** Temperature dependence of the $^1H$ NMR (500-MHz) spectrum of octaphenylferrocene. Temperatures are in degrees centigrade.

c and z to meta protons. To test this model the selectively deuterated complex V was synthesized. The $^1H$ NMR spectrum of V (Figure 5) allows resonances a, b, and c (relative areas 2:1:2) to be assigned to phenyl rings 2 and 5; resonances x, y, and z are not present and must be assigned to phenyl rings 3 and 4 (rings are numbered according to Figure 1).

The 500-MHz $^1H$ spectra of III obtained between 20 and −95 °C are displayed in Figure 6. Beginning at −20 °C doublet x begins to recede and at −95 °C two new resonances, each integrating to one proton, appear at 6.50 and 7.62 ppm. These absorptions are centered about doublet x in the 20 °C spectrum. The triplet z for the meta protons associated with the same rings separates into two new resonances (6.8 and 6.9 ppm) between −80 and −95 °C. A second striking feature of these spectra is the downfield shift of the cyclopentadienyl singlet by 0.09 ppm per 20 °C temperature drop. An explanation for these observations invokes slowed phenyl ring rotation. At 20 °C, all phenyl groups rotate rapidly on the NMR time scale. As the solution is cooled the phenyl group rotation slows, particularly for rings 3 and 4.

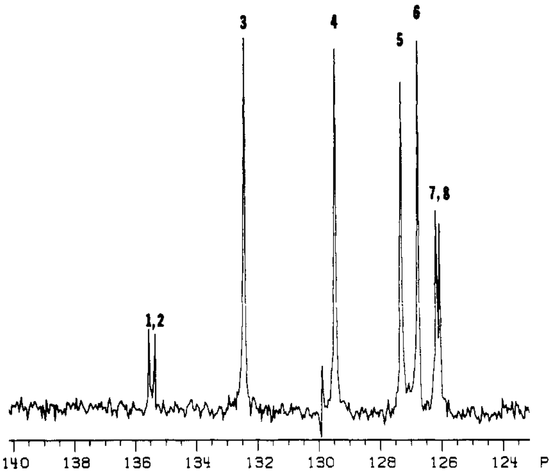

**Figure 7.** The $^{13}C\{^1H\}$ NMR spectrum of the aromatic region of octaphenylferrocene in THF-$d_8$ solvent.

That the ortho and meta resonances (x and z) for rings 3 and 4 each separate into two new resonances suggests that these phenyl groups freeze out in a conformation whereby both rings lie roughly perpendicular to the cyclopentadienyl ring plane. Thus, the ortho and meta protons on opposite sides of the phenyl rings become inequivalent since half point inside the sandwich and half outside the sandwich. This allows phenyl groups 2 and 5 to become coplanar with the cyclopentadienyl ring (as partially occurs in the solid-state structure). The striking downfield shift of the cyclopentadienyl proton can be attributed to deshielding from ring currents of the adjacent coplanar phenyl rings.

The cyclopentadienyl proton resonance also splits slightly when the temperature decreases. This splitting may arise from the effect of slowed phenyl ring rotation. No evidence is observed for restricted rotation of the two cyclopentadienyl rings above −95 °C.

From the spectra in Figure 6 the rate of phenyl ring rotation and the free energy of activation at the coalescence temperature for doublet x (ortho phenyl ring protons) can be estimated. A peak separation of 550 Hz at −95 °C yields 1200 Hz for the rate of phenyl ring rotation at coalescence (ca. −65 °C) (eq 3).[32] From this value of $\Delta\nu$ the activation

$$k_c = (\pi/\sqrt{2})(\Delta\nu) \qquad (3)$$

free energy can be estimated (eq 4)[32] to be 9 ± 1 kcal/mol

$$\Delta G_c^{\ddagger} = (4.575 \times 10^{-3})T[9.972 + \log(T/\Delta\nu)] \qquad (4)$$

at coalescence. A similar calculation for triplet z also yields 9 kcal/mol for the activation barrier; however, this value is less certain because a limiting spectrum was not obtainable.

The $^{13}C$ NMR spectrum of III was also examined (Figure 7). Aromatic regions of the $^{13}C$ NMR spectra of (phenylcyclopentadienyl)(cyclopentadienyl)iron(II)[33] and bis(diphenylcyclopentadienyl)iron(II)[34] have been assigned, with the results in disagreement. By selectively decoupling each of the four proton multiplets of III and recording the

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**Table VIII.** **$^{13}$C NMR Resonance Assignments of $(C_5HPh_4)_2Fe$ in THF and $CH_2Cl_2$ Solutions**

| | assignt | | position (ppm) | |
|---|---|---|---|---|
| resonance | carbon type | position[a] | THF | $CH_2Cl_2$ |
| 1 | quaternary | 2,5 p | 135.54 | 133.85 |
| 2 | quaternary | 3,4 p | 135.34 | |
| 3 | ortho | 3,4 p | 132.41 | 130.52 |
| 4 | ortho | 2,5 p | 129.44 | 127.65 |
| 5 | meta | 2,5 p | 127.28 | 126.22 |
| 6 | meta | 3,4 p | 126.73 | 125.44 |
| 7 | para | 2,5 p | 126.13 | 124.87 |
| 8 | para | 3,4 p | 126.03 | |
| quaternary m | | 3,4 c | 91.98 | 92.39 |
| quaternary n | | 2,5 c | 86.11 | 86.95 |
| methine | | | *b* | 67.24 |

[a] p = phenyl ring; c = cyclopentadienyl ring. [b] Obscured by solvent resonance.

$^{13}$C NMR spectra, the following assignments were made: resonance 3 (ortho carbon, phenyl rings 3 and 4), resonance 4 (ortho, rings 2 and 5), resonance 5 (meta, rings 2 and 5), resonance 6 (meta, rings 3 and 4), resonance 7 (para, rings 2 and 5), and resonance 8 (para, rings 3 and 4). Resonances 1 and 2 are assigned as the phenyl quaternary carbons because of their low intensity and downfield location. The $^{13}C\{^1H\}$ NMR of selectively deuterated V was required to assign these resonances. Long-range deuterium coupling resulted in only one sharp resonance for the quaternary carbon in the protiophenyl ring. Resonance 7 arises from the quaternary carbons on rings 2 and 5 and resonance 8 from those of rings 3 and 4. Low-temperature $^{13}$C NMR spectra did not provide further information about the motional process.

Because of solvent overlap, assignment of the cyclopentadienyl carbons (Table VIII) was made in $CH_2Cl_2$ solvent. The furthest downfield resonance can be assigned to the unsubstituted carbon because of its chemical shift and high intensity. From the $^{13}$C NMR spectra of III and V in THF, resonances m and n are assigned to carbons 3 and 4 and carbons 2 and 5, respectively. The detailed assignments proposed here are in substantial agreement with the those proposed for bis(diphenylcyclopentadienyl)iron(II).[34]

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**Registry No.** I, 15570-45-3; II, 58081-02-0; III, 12151-36-9; IV, 101200-07-1; V, 101200-08-2; $Ph_4C_5O$, 479-33-4.

**Supplementary Material Available:** Tables of structure factors, bond distances and angles, anisotropic temperature factors, and hydrogen atom coordinates (23 pages). Ordering information is given on any current masthead page.

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# Electron Transfer in Organometallic Clusters. 8.[1] Electron-Transfer Chain Catalyzed and Thermal Reactions of Polydentate Ligands with $RCCo_3(CO)_9$

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A comparative study of the electron-transfer chain catalyzed (ETC) and thermal reactions of the polydentate ligands dppm, dppe, ttas, and tpme with $RCCo_3(CO)_9$ (R = Ph, Me) in $CH_2Cl_2$, THF, acetone, and $CH_3CN$ is described. The structural types $RCCo_3(CO)_8(L\text{–}L)$, $RCCo_3(CO)_7(L\text{–}L)$ ($L\text{–}L \equiv$ dppm, dppe), $[RCCo_3(CO)_8]_2(\mu\text{-dppe})$, $RCCo_3(CO)_6(dppm)_2$, $RCCo_3(CO)_5(dppm)_2$, $[RCCo_3(CO)_8]_2$tpme, $RCCo_3(CO)_7$tpme, and $RCCo_3(CO)_6$tpme were characterized by IR and $^1$H, $^{13}$C, and $^{31}$P NMR spectroscopy and for $[PhCCo_3(CO)_8]_2(\mu\text{-dppe})$ by X-ray crystallography ($a = 11.888$ (3) Å, $b = 13.059$ (3) Å, $c = 10.967$ (1) Å, $\alpha = 97.64$ (1)°, $\beta = 118.64$ (1)°, $\gamma = 93.74$ (2)°, triclinic $P\bar{1}$, $Z = 1$). R = 0.0405 for 3091 ($I > 3\sigma(I)$) reflections.

Electron-transfer chain catalyzed (ETC) reactions offer a rapid energy-efficient method for the activation of metal carbonyl clusters to nucleophilic substitution.[2–4] Parameters influencing the efficiency of these reactions with monodentate ligands have been delineated and include the basicity and size of the nucleophile and the kinetic stability of the intermediate cluster radical anion.[3,5] In order to study the stereochemical nuances and synthetic utility of these ETC reactions in more detail, we have turned to polydentate nucleophiles. In principle the decrease in catalytic efficiency with increasing CO substitution noted in the reactions with monodentate ligands should enable controlled selective syntheses of partially or fully ligated polydentate derivatives—an example has been given in a preliminary communication.[7] Furthermore, the $S_{RN}1$

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