Steric and Electronic Interactions between Cofacial Metallocene Rings

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As part of a study of interactions between metallocenes, held so that two cyclopentadienyl rings are constrained to be proximate and facing one another, 1,8-diruthenocenylnaphthalene (**1b**) has been prepared and its crystal structure has been determined. This structure is shown to be close to that of 1,8-diferrocenylnaphthalene (**1a**) reported earlier, especially in respect to the dihedral angle between the substituted cyclopentadienyl and naphthalene ring planes and the splay angle between the two substituted cyclopentadienyl rings. Both of these distortions are significantly diminished in the monocation derived from **1a**, suggesting that there is a significant decrease in electron density on the cyclopentadienyl rings on oxidation of ferrocene to a ferricenium cation, consistent with theoretical analyses.

Introduction

We recently reported the synthesis of 1,8-diferrocenylnaphthalene (**1a**) through palladium-catalyzed coupling of ferrocenyl zinc chloride with 1,8-diiodonaphthalene.[1] This substance represents the first member of a family of "face to face" metallocenes designed to serve as monomeric model compounds for their polymeric analogues **2** whose mixed-valence state might be expected to have interesting physical properties.

1a, M = Fe
b, M = Ru

2
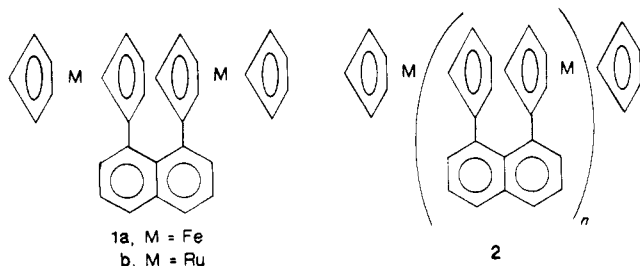
Since π-orbital interactions across the cofacial cyclopentadienyl rings in such a polymeric system would be important for valence band formation, the crystal structure of the model compound **1a** was determined. This showed a highly distorted structure in which the two opposed cyclopentadienyl rings were found to be rotated 45–47°

from a conformation perpendicular to the naphthalene best plane. Such a rotation, together with a splaying of these rings, so that the dihedral angle between them is 29.1 (1)°, would be expected to lower their repulsive π-orbital interactions. We were, however, surprised to find that this ring rotational angle was significantly greater for **1a** than has been observed in analogous π-cofacial systems such as 1,8-diphenylnaphthalene[2] (**3**), 5,6-diphenylacenaphthene[3] (**4**), or 1,4,5,8-tetraphenylnaphthalene[4] (**5**) (Table VII) and suggested that nonbonding interactions between β-naphthalene hydrogen atoms and hydrogen atoms on the unsubstituted cyclopentadienyl ring in **1a** might be responsible for this difference. In order to test this hypothesis, we undertook the synthesis and crystal structure determination of the analogous 1,8-diruthenocenylnaphthalene (**1b**), since the distance separating the two cyclopentadienyl rings in ruthenocene is more than 0.3 Å larger than it is in ferrocene.[5] Consequently, steric interactions such as those described above would be expected to be significantly lowered. The crystal structure of the monocation **1a⁺**, derived by one electron oxidation of **1a**, has also been determined in order to probe the effect of such

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an electronic change on molecular distortions. This report provides an account of these findings.

Experimental Section

All reactions were carried out under an atmosphere of dry nitrogen or argon. Air- and/or moisture-sensitive reagents were handled by using standard syringe transfer techniques and flasks were capped with rubber septa. Flexible double-tipped needles (cannula) were used to transfer larger amounts (>10 mL) of liquid or reagents. Solvents were dried by standard procedures and stored under nitrogen. Tetrahydrofuran was freshly distilled from sodium benzophenone ketyl prior to use. Reactions were monitored by thin-layer chromatography on silica gel slides and preparative plates (Analtech Silica Gel GF, 1000 μm) were used to isolate products. Ruthenocene (Polysciences) and N,N,N',N'-tetramethylethylenediamine (TMEDA, Aldrich) were used as purchased. Butyllithium (2.5 M solution in hexanes, Aldrich) was assayed by titration with 2-butanol and 2,2'-dipyridyl as indicator. Anhydrous zinc chloride (Alfa, ultrapure) or a 1.0 M solution in diethyl ether (Alfa) was used. 1,8-Diiodonaphthalene was prepared as described in the literature.[6]

NMR spectra were recorded on a Varian XL300 spectrometer (NIH-1-S10RR01493-01-A1) and referenced to solvent CDCl$_3$. A Varian EM-390 spectrometer was used for integration measurements. Mass spectra were recorded at the MIT mass spectrometry laboratory on a Varian MAT 731 high-resolution mass spectrometer with a combined EI/FI/FD ion source and FAB gun. Melting points were determined under a nirogen atmosphere on a Kofler hot stage and are uncorrected. Elemental analyses were performed by E and R Microanalytical Laboratory, Inc., Corona, NY.

Preparation of 1,8-Diruthenocenylnaphthalene (1b). To ruthenocene (297 mg, 1.28 mmol) suspended in 15 mL of hexane was added via syringe a solution of *n*-butyllithium (1.14 mL, 2.57 mmol) and TMEDA (0.39 mL, 2.57 mmol) in 5 mL of hexane. After the solution was stirred overnight at room temperature, the flask, which now contained a suspension of 1,1'-dilithioruthenocene–TMEDA, was cooled in an ice bath. The supernatant was removed by cannula filtration, and the residual pale yellow solid was dissolved in 9 mL of THF. The supernatant was hydrolyzed with 1 N HCl. The organic layer was dried with Na$_2$SO$_4$ and evaporated to give 40 mg of recovered ruthenocene. Thus, no more than 257 mg (1.11 mmol) of ruthenocene was converted. A solution of anhydrous zinc chloride (302 mg, 2.22 mmol) in 10 mL of THF was added slowly to the dilithioruthenocene solution at 0 °C. A transient precipitate formed but redissolved during the addition. The dark yellow turbid solution was stirred for 3 h at room temperature and then was transferred by cannula to an addition funnel on top of a three-neck flask charged with 1,8-diiodonaphthalene (129 mg, 0.34 mmol) and Pd(dppf)Cl$_2$[12] (27 mg, 0.037 mmol) in 20 mL of THF. The solution containing the ruthenocenylzinc chloride was added dropwise over 0.5 h at 0 °C. The amber-colored reaction mixture was allowed to warm to room temperature and was then refluxed overnight. TLC monitoring (silica, hexane–CH$_2$Cl$_2$, 4:3) showed three major components: the two unreacted starting materials and **1b**. When successive TLC tests indicated no change in product profile, the reaction mixture was hydrolyzed with 1 N HCl. The dark brown organic layer was evaporated to give a brown oil with dispersed water droplets. This residue was taken up in CH$_2$Cl$_2$, washed with water, and dried over MgSO$_4$. Upon evaporation to near dryness a sand-colored precipitate formed which was separated, washed with ether, and dried in vacuo. This product, shown by TLC to be **1b** with stationary impurities, was dissolved in hexane–CH$_2$Cl$_2$ (1:1) and filtered through a short column of silica (Merck, Grade 60) under nitrogen overpressure. Pale yellow crystals (67 mg) were obtained from the filtrate. Evaporation of the supernatant gave a dark brown semisolid material. Preparative TLC on silica with hexane–CH$_2$Cl$_2$ (3:2) afforded 48 mg (37%) diiodonaphthalene and an additional 38 mg of **1b**. Barely detectable traces of oligomers were not isolated. The combined yield of 1,8-diruthenocenyl naphthalene was 105 mg (85% based on diiodo-

naphthalene consumed). Recrystallization from CH$_2$Cl$_2$–ether gave pale yellow flat prisms, which darkened without melting above 210 °C: ^{1}H NMR (CDCl$_3$) δ 4.33 (t, J = 1.8 Hz, 4, H$_{3,4}$-Cp), 4.36 (s, 10, Cp), 4.66 (t, J = 1.8 Hz, 4, H$_{2,5}$-Cp), 7.28 (t, J = 7.7 Hz, 2, H$_{3,6}$-Ar), 7.67 (dd, J = 8.1, 1.5 Hz, 2, H$_{2,7}$-Ar), 7.87 (dd, J = 7.5, 1.5 Hz, 2, H$_{4,5}$-Ar); ^{13}C NMR (CDCl$_3$): 69.17, 71.47, 74.67, 124.01, 127.48, 134.21 ppm; MS (FD$^+$), M$^+$ 588, M^{2+} 294. Anal. Calcd for C$_{30}$H$_{24}$Ru$_2$: C, 61.34; H, 4.09. Found: C, 61.45; H, 3.97.

In a similar reaction the ratio of diiodonaphthalene versus ruthenocene-derived Zn reagent was held to about 1:1. The TLC profile of the crude product indicated several oligomeric fractions, although as minor components. Separation by preparative TLC yielded unreacted 1,8-diiodonaphthalene (31%), ruthenocene, a trace of 1-iodo-8-ruthenocenylnaphthalene, product **1b** (20% based on diiodonaphthalene consumed), and two oligomeric fractions (yellow solids, 5 mg each) containing the oligomer **9** (MS (FAB) M$^+$ 934 C$_{50}$H$_{38}$Ru$_3$) and the oligomer **10** (M$^+$ 1298 C$_{70}$H$_{52}$Ru$_4$).

Preparation of the Salt 1,8-Diferrocenylnaphthalene Tetrafluoroborate. Silver tetrafluoroborate (46 mg, 0.23 mmol), handled in a glovebox, was dissolved in 3.5 mL of anhydrous ether. This solution was added dropwise to 1,8-diferrocenylnaphthalene (116 mg, 0.23 mmol) in 12 mL of CH$_2$Cl$_2$. The orange solution turned immediately brown and turbid. After the solution was stirred for 1.5 h at room temperature, the suspension was diluted with methanol and filtered through Celite to remove the finely divided silver metal. The filtrate was evaporated, and the brown residual solid was dissolved in the minimum amount of CH$_2$Cl$_2$. Crystallization by vapor-phase diffusion with ether gave a first crop of 70 mg of diferrocenylnaphthalene tetrafluoroborate: black-brown crystals; mp 197–199 °C. Later crops that crystallized from CH$_2$Cl$_2$–ether contained traces of unoxidized **1a**. Anal. Calcd for C$_{30}$H$_{24}$Fe$_2$BF$_4$: C, 61.82; H, 4.12. Found: C, 61.26; H, 4.19.

General Procedure for Assaying Metalated Ferrocenes. Dilithioferrocene–TMEDA complex was prepared from ferrocene and 2 equiv each of *n*-butyllithium and TMEDA in hexane.[7] Cannula filtration removed the supernatant solution from the precipitated dilithioferrocene–TMEDA complex, which was then dissolved in THF. This solution was hydrolyzed with 1 N DCl in D$_2$O under argon, and solvent was then removed. The residue was taken up in hexane and the solution filtered through alumina (neutral, activity IV). After evaporation of the solvent, the deuteriated ferrocene was dried in vacuo.

Ferrocenylzinc chloride reagents were prepared as follows: Dilithioferrocene was prepared as above, except that the supernatant hexane solution was hydrolyzed and recovered ferrocene was isolated, in order to obtain a more exact measure of the amount of ferrocene converted to the dilithio derivative. The dilithioferrocene was taken up in THF and a standard zinc chloride solution (1 M in diethyl ether) was added dropwise to it. The resulting solution was stirred for 2.5 h at room temperature, hydrolyzed with D$_2$O, and worked up as described above.

NMR samples were prepared with 44 mg (0.237 mmol) of deuteriated ferrocene in 0.70 mL of CDCl$_3$ with 25 mg (0.237 mmol) of toluene as internal standard. Standard NMR spectra of nondeuteriated ferrocene were also determined to calibrate the integrations.

Structure Determination of 1b. Single crystals were grown from methylene chloride–ether solutions by the vapor phase diffusion method. Laue photographs and a preliminary X-ray photographic study indicated the crystal to be of excellent quality. The crystal was then transferred to a Supper No. 455 goniometer and optically centered on a Syntex P2$_1$ diffractometer. Operations were performed as described previously.[8] The analytical scattering factors of Cromer and Waber were used; real and imaginary components of anomalous scattering for Fe were included in the calculations.[9] All computational work was carried out on a NOVA 1200 computer using the Syntex XTL package. Details of the

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(7) Bednarik, L.; Neuse, E. *J. Organomet. Chem.* **1979**, *168*, C8. See also: Rausch, M. D.; Ciappenelli, D. J. *J. Organomet. Chem.* **1967**, *10*, 127. Bishop, J. J.; Davison, A.; Katcher, M. L.; Lichtenberg, D. W.; Merrill, R. E.; Smart, J. C. *J. Organomet. Chem.* **1971**, *27*, 241.

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(9) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV: pp 99–101, 148–150.

Table I. Data for the X-ray Diffraction Study of 1,8-Diruthenocenylnaphthalene

(A) Crystal Data at 21 (1) °C

cryst system: monoclinic $Z = 4$

space group: $C2/c$ [C_{2h}^6, No. 15]　　cryst size: 0.055 × 0.11 × 0.65 mm

a = 17.853 (4) Å

b = 10.238 (2) Å　　　fw: 586.7

c = 12.083 (3) Å　　　ρ_{obsd} = 1.76 (1)^a g cm^{-3}

β = 90.94 (1)°　　　ρ_{calcd} = 1.72 g cm^{-3}

V = 2208 (1) Å^3　　　μ = 13.5 cm^{-1} (MoK$\bar{\alpha}$)

cell constant determination: 12 pairs ±(hkl) and refined 2θ, ω, χ values in the range 28 ≤ |2θ| ≤ 31° (λ(Mo K$\bar{\alpha}$) = 0.710 73 Å)

(B) Measurement of Intensity Data

radiatn: Mo K$\bar{\alpha}$, graphite monochromator

reflctns measd: h, k, ±l (to 2θ = 54°)

scan type, speed: θ-2θ, 1.95–3.91°/min

scan range: symmetrical, [1.8 ± Δ($\alpha_2 - \alpha_1$)]°

no. of reflctns measd: 2511; 2435 in unique set

std reflctns: 12,0,2, 17$\bar{2}$, 22$\bar{8}$ measd after each 60 reflctns; variation < ±3σ(I) for each

abs correctn: empirical, using 00$\bar{2}$, 00$\bar{4}$, 00$\bar{6}$, 0,0,$\overline{10}$ reflctns, normalized transmissn factors 0.868–1.000

statistical informatn: R_s = /.024; R_{av} = 0.006 (0kl reflctns)

(C) Solution and Refinement, with 1811 Data for Which $F > 3.92\sigma(F)$

weighting of reflctns: as before,^{b} p = 0.035

soln: Patterson, difference Fourier, routine

refinement^c: full-matrix least squares, with anisotropic temperature factors for Ru, C atoms; H atoms at fixed positions (0.95 Å); R = 0.033; R_w = 0.044; SDU = 0.953; R (structure factor calcn with all 2435 reflctns) = 0.057

final difference map: 6 peaks, 0.32–0.59 e/Å^3 near unsubstituted Cp or Ru; other peaks random and ≤0.3 e/Å^3

weighting scheme analysis: no systematic dependence on magnitude of |F_o|, (sin θ)/λ, or indices

^{a} Measured by neutral buoyancy in aqueous KI.　^{b} Foxman, B. M.; Mazurek, H. *Inorg. Chem.* **1979**, *18*, 113 and references therein. ^{c} R_s = $\sum(\sigma(|F_o|)/\sum|F_o|$; R_{av} = $\sum|I - I_{av}|/\sum I$. R = $\sum||F_o| - |F_c||/\sum|F_o|$; R_w = $\{\sum w[|F_o| - |F_c|]^2/\sum w|F_o|^2\}^{1/2}$. SDU = $\{\sum w[|F_o| - |F_c|]^2/(m - n)\}^{1/2}$, where m (= 1811) is the number of observations and n (= 146) is the number of parameters.

Table II. Atomic Coordinates for 1,8-Diruthenocenylnaphthalene^{a,b}

atom	x	y	z	B, Å^2
Ru	0.18176 (2)	0.05443 (4)	0.34979 (3)	2.749 (8)
C(1)	0.0676 (2)	−0.0196 (4)	0.3219 (4)	2.36 (8)
C(2)	0.0675 (2)	0.0792 (5)	0.4057 (4)	3.1 (1)
C(3)	0.0911 (3)	0.1971 (5)	0.3596 (5)	3.8 (1)
C(4)	0.1084 (2)	0.1735 (5)	0.2459 (5)	3.8 (1)
C(5)	0.0944 (2)	0.0404 (5)	0.2241 (3)	2.88 (9)
C(6)	0.2796 (4)	0.0933 (9)	0.450 (1)	8.6 (3)
C(7)	0.2537 (4)	−0.030 (1)	0.4763 (6)	7.2 (2)
C(8)	0.2602 (3)	−0.1019 (6)	0.3842 (6)	5.2 (2)
C(9)	0.2870 (3)	−0.0309 (8)	0.2995 (5)	5.5 (2)
C(10)	0.3007 (3)	0.100 (1)	0.341 (1)	8.9 (3)
C(11)	0.0453 (2)	−0.1587 (4)	0.3336 (4)	2.59 (8)
C(12)	0.0734 (3)	−0.2307 (5)	0.4205 (4)	3.7 (1)
C(13)	0.0629 (3)	−0.3660 (6)	0.4281 (6)	4.9 (1)
C(14)	0.0296 (3)	−0.4306 (5)	0.3421 (6)	5.0 (1)
C(15)	0.000	−0.3625 (7)	0.250	3.9 (2)
C(16)	0.000	−0.2216 (6)	0.250	2.6 (1)

^{a} Atoms refined by using anisotropic temperature factors are given in the form of the isotropic equivalent displacement parameter defined as $1.33[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos \gamma)B_{12} + ac(\cos \beta)B_{13} + bc(\cos \alpha)B_{23}]$.　^{b} Numbers in parentheses in this and following tables are estimated standard deviations in the least significant digit.

structure analysis, in outline form, are presented in Table I. Atomic coordinates for all non-hydrogen atoms appear in Table II.

Structure Determination of 1a$^+$. Single crystals were grown from methylene chloride–ether solution by the vapor-phase

Table III. Data for the X-ray Diffraction Study of [(C$_{10}$H$_9$Fe)$_2$C$_{10}$H$_6$]BF$_4$

(A) Crystal Data at 21 (1) °C

cryst system: monoclinic $Z = 4$

space group: $P2_1/c$ [C_{2h}^5; No. 114]　　cryst size: 0.084 × 0.13 × 0.55 mm

a = 13.349 (4) Å

b = 10.101 (4) Å　　　fw: 583.02

c = 19.776 (6) Å　　　ρ_{obsd} = 1.57 (1)^a g cm^{-3}

β = 113.60 (3)°　　　ρ_{calcd} = 1.585 g cm^{-3}

V = 2444 (3) Å^3　　　μ = 12.3 cm^{-1} (Mo K$\bar{\alpha}$)

cell constant determination: 12 pairs ±(hkl) and refined 2θ, ω, χ values in the range 18 ≤ |2θ| ≤ 23° (λ(MoK$\bar{\alpha}$) = 0.710 73 Å)

(B) Measurement of Intensity Data

radiatn: Mo K$\bar{\alpha}$, graphite monochromator

reflctns measd: h, k, ±l (to 2θ = 45°)

scan type, speed: θ-2θ, 1.95–3.91°/min

scan range: symmetrical, [1.8 + Δ($\alpha_2 - \alpha_1$)]°

no. of reflctns measd: 3356; 3194 in unique set

std reflctns: 020, 60$\bar{4}$, 008 measd after each 60 reflctns; variation < ± 3σ(I) for each

abs correctn: empirical, using 020, 040, 162 reflections, normalized transmissn factors 0.894–1.000

statistical informatn: R_{av} = 0.018 (0kl reflctns)

(C) Solution and Refinement, with 2144 Data for Which $I > 1.96\sigma(I)$

weighting of reflctns: as before,^{b} p = 0.040

soln: Patterson, difference Fourier, routine

refinement^c: full-matrix least squares, with anisotropic temperature factors for Fe, Cp C atoms; isotropic temperature factors for B, naphthalene C atoms; H atoms at fixed positions (0.95 Å); R = 0.052; R_w = 0.050; SDU = 1.373; R (structure factor calcn with all 3194 reflctns) = 0.093

final difference map: 4 peaks, 0.34–0.44 e/Å^3 near BF$_4^-$; other peaks random and ≤0.33 e/Å^3

weighting scheme analysis: no systematic dependence on magnitude of |F_o|, (sin θ)/λ, or indices

^{a} Measured by neutral buoyancy in carbon tetrachloride–heptane.　^{b} Foxman, B. M.; Mazurek, H. *Inorg. Chem.* **1979**, *18*, 113 and references therein. ^{c} R_{av} = $\sum|I - I_{av}|/\sum I$; R = $\sum||F_o| - | F_c||/\sum|F_o|$; R_w = $\{\sum w[|F_o| - | F_c|]^2/\sum w|F_o|^2\}^{1/2}$. SDU = $\{\sum w[|F_o| - |F_c|]^2/(m - n)\}^{1/2}$, where m (= 2144) is the number of observations and n (= 279) is the number of parameters. The structure was refined by using anisotropic temperature factors for Fe, F and Cp carbon atoms only owing to (a) a low (7.7:1) data to parameter ratio and (b) the lack of evidence (from difference Fourier syntheses) for significant residual electron density near the naphthalene C atoms.

diffusion method, as dark brown rectangular platelets. Laue photographs and a preliminary X-ray photographic study indicated the crystal to be of good quality. The crystal was then transferred to a Supper No. 455 goniometer and optically centered on a Syntex P2$_1$ diffractometer. Operations were performed as described previously.[8] The analytical scattering factors of Cromer and Waber were used; real and imaginary components of anomalous scattering for Fe were included in the calculations.[9] All computational work was carried out on a VAX 8600 computer using the Enraf-Nonius SDP software package. Details of the structure analysis, in outline form, are presented in Table III. Atomic coordinates for all non-hydrogen atoms appear in Table IV.

Electrical Conductivity. Conductivity measurements on complex 1a$^+$ were made by using an instrument built by Research Specialities, Chicago, IL; the system samples at a low AC frequency, 27 Hz, to minimize possible polarization problems associated with a DC instrument but with electronic circuitry designed to remove capacitive effects.[10] Sample sizes were measured with a calibrated reticle on a Bausch and Lomb Stereozoom 7 microscope. Both pressed pellet and single crystal samples were tested, but no measurable conductivities were found in either case, setting an upper limit for the conductivity of 1 × 10^{-6} Ω^{-1} cm^{-1}.

(10) Phillips, T. E.; Anderson, J. R.; Schramm, C. J.; Hoffman, B. M. *Rev. Sci. Instrum.* **1979**, *50*, 263.

### Table IV. Atomic Coordinates for [(C$_{10}$H$_9$Fe)$_2$C$_{10}$H$_6$]BF$_4$[a]

atom	x	y	z	B, Å^2
Fe(1)	0.87792 (6)	0.891 (1)	0.08455 (4)	3.28 (2)
Fe(2)	1.37541 (6)	0.2300 (1)	0.31159 (5)	3.64 (2)
F(1)	0.4457 (4)	0.3812 (5)	0.1498 (2)	8.3 (1)
F(2)	0.5904 (4)	0.2546 (8)	0.1849 (3)	13.6 (2)
F(3)	0.4451 (5)	0.1912 (6)	0.0927 (4)	11.9 (2)
F(4)	0.5387 (4)	0.3579 (5)	0.0799 (3)	11.5 (2)
C(1)	1.2131 (4)	0.1515 (6)	0.2876 (3)	3.2 (2)
C(2)	1.2747 (4)	0.06282 (8)	0.2596 (3)	4.6 (2)
C(3)	1.3037 (5)	0.1441 (8)	0.2095 (4)	5.2 (2)
C(4)	1.2616 (5)	0.2744 (9)	0.2071 (3)	5.2 (2)
C(5)	1.2082 (4)	0.2789 (7)	0.2569 (3)	4.2 (2)
C(6)	1.5400 (5)	0.1957 (8)	0.3463 (4)	5.0 (2)
C(7)	1.5100 (5)	0.1702 (8)	0.4052 (4)	5.0 (2)
C(8)	1.4691 (5)	0.2906 (8)	0.4212 (3)	4.8 (2)
C(9)	1.4765 (5)	0.3866 (7)	0.3728 (4)	5.1 (2)
C(10)	1.5204 (5)	0.3292 (8)	0.3266 (4)	5.5 (2)
C(11)	0.9866 (4)	0.1430 (6)	0.1889 (3)	3.0 (1)
C(12)	1.0189 (4)	0.0211 (6)	0.1671 (3)	3.3 (2)
C(13)	1.0341 (5)	0.0437 (8)	0.1003 (3)	4.3 (2)
C(14)	1.0114 (5)	0.1789 (7)	0.0822 (3)	4.9 (2)
C(15)	0.9807 (5)	0.2411 (7)	0.1357 (3)	4.1 (2)
C(16)	0.7789 (5)	−0.0198 (9)	−0.0051 (4)	6.0 (2)
C(17)	0.7567 (5)	0.1168 (9)	−0.0166 (4)	6.6 (2)
C(18)	0.7235 (5)	0.1605 (8)	0.0403 (4)	6.4 (2)
C(19)	0.7279 (5)	0.0516 (8)	0.0838 (4)	5.4 (2)
C(20)	0.7623 (5)	−0.0577 (8)	0.0570 (4)	5.6 (2)
C(21)	1.1680 (4)	0.1121 (6)	0.3421 (3)	3.0 (1)
C(22)	1.2395 (5)	0.0663 (7)	0.4099 (3)	4.1 (1)
C(23)	1.2091 (5)	0.0498 (7)	0.4692 (3)	4.6 (2)
C(24)	1.1061 (5)	0.0827 (7)	0.4602 (3)	3.9 (1)
C(25)	1.0258 (5)	0.1247 (6)	0.3911 (3)	3.4 (1)
C(26)	0.9190(5)	0.1567 (7)	0.3834 (3)	4.3 (1)
C(27)	0.8432 (5)	0.1962 (7)	0.3167 (3)	4.5 (2)
C(28)	0.8686 (5)	0.1961 (6)	0.2542 (3)	3.9 (1)
C(29)	0.9702 (4)	0.1611 (6)	0.2585 (3)	3.0 (1)
C(30)	1.0557 (4)	0.1339 (6)	0.3291 (3)	3.0 (1)
B	0.5044 (7)	0.294 (1)	0.1275 (5)	5.6 (2)

[a] Atoms refined by using anisotropic temperature factors are given in the form of the isotropic equivalent displacement parameter defined as $1.33[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos \gamma)B_{12} + ac(\cos \beta)B_{13} + bc(\cos \alpha)B_{23}]$.

Pressed pellets were run by using the four-probe van der Pauw geometry. Six different single crystals (ranging from 1.0 to 1.5 mm in length and averaging 0.05 × 0.03 mm in cross section) were mounted for four-probe measurement along the needle (crystallographic b) axis. Shining light on the crystals also gave unmeasurable resistances, so that a significant photoconductivity was not observed.

Results and Discussion

The synthetic approach used for the preparation of **1a**, employing palladium-catalyzed coupling of a metallocenylzinc chloride **6** with 1,8-diiodonaphthalene (**7**), was used for the preparation of **1b**.
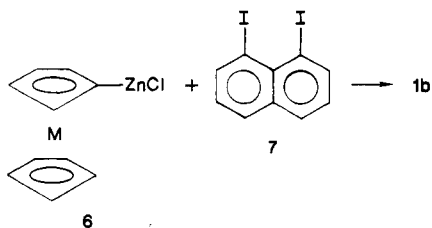
Since bromoruthenocene, required in the preparation of the metalated reactant, is available only in low yield through ruthenocenylboric acid,[11] we chose instead to examine an alternative route. Dilithioruthenocene is readily

Table V. Deuterium Incorporation on Quenching Metalated Ferrocenes with D$_2$O

compound	rel proton integratns[a]		
	Me[b]	Cp	aromatic[b]
1,1′-dilithioferrocene–TMEDA complex (8)	3.0	7.9	4.7
8 + 4 equiv of ZnCl$_2$	3.0	10.1	4.9
8 + 2 equiv of ZnCl$_2$	3.0	8.7	4.8
8 + 1 equiv of ZnCl$_2$	3.0	8.3	4.9

[a] Average of four integrations. [b] Internal standard toluene.

available as the tetramethylethylenediamine adduct by direct metalation of ruthenocene,[7] and experience in our laboratory had shown that 1,1′-dilithioferrocene–TMEDA (**8**) on treatment with zinc chloride could be made to give good yields of **1a**. Furthermore, the small amount of oligomeric product formed in these reactions was readily separable from **1a**.

Here too, we found that conversion of 1,1′-dilithioruthenocene to the zinc reagent by treatment with 2 molar equiv of zinc chloride, and subsequent reaction of this reagent with 1,8-diiodonaphthalene in the presence of a catalytic amount of dichloro[1,1′-bis(diphenylphosphino)ferrocene]palladium[12] gave good yields of **1b**. Indeed, when the ratio of the ruthenocenylzinc reagent to diiodonaphthalene was 3:1, **1b** is obtained in 85% yield, corrected for recovered diiodonaphthalene. A trace amount of dimeric product **9** was detectable by TLC from these reactions. The amount of this substance, together with trimer **10**, increased significantly when the ratio of the ruthenocenyl reagent to diiodonaphthalene was reduced to 1:1.

9, n = 2
10, n = 3
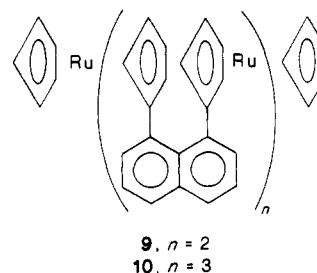
The preparation and chemistry of these oligomeric metallocenes forms the subject matter of a future report, but the general observations summarized above suggest that small amounts of water or of zinc hydroxide present in the zinc reagent are responsible for the unexpected coupling products. Some evidence on this point was obtained by a comparison of the integrated cyclopentadienyl proton resonances obtained when solutions of 1,1′-dilithioferrocene–TMEDA complex were quenched with D$_2$O before and after treatment with increasing amounts of commercial samples of anhydrous zinc chloride in diethyl ether. These results are summarized in Table V and suggest the presence of a proton source in the zinc chloride solutions, which at the level of 4 molar equiv of zinc salt/mol of dilithioferrocene is sufficient to completely quench the metalated ring.

1,8-Diruthenocenylnaphthalene is a pale yellow solid, which darkens progressively above 210 °C without melting. The molecular structure of **1b** is shown in Figure 1, which also gives the numbering scheme. The molecule has crystallographic C$_2$ symmetry; atoms C(15) and C(16) are located on the crystallographic C$_2$ axis. Selected bond lengths and angles, which lie within normal ranges, are

(11) Nesmeyanov, A. N.; Lubovich, A. A.; Gubin, S. P., *Izv. Akad. Nauk SSSR, Ser. Khim.* **1972**, *8*, 1823.

(12) Hayasaki, T.; Konishi, M.; Kumada, M. *Tetrahedron Lett.* **1979**, 1871. The phosphine is available from Aldrich Chemical Co.

Table VI. Selected Bond Lengths (Å) and Angles (deg) for 1,8-Diruthenocenylnaphthalene

atom 1	atom 2	dist	atom 1	atom 2	dist
Ru	C(1)	2.195 (4)	Ru	C(10)	2.177 (6)
Ru	C(2)	2.173 (4)	C(1)	C(11)	1.486 (6)
Ru	C(3)	2.184 (5)	C(11)	C(12)	1.371 (7)
Ru	C(4)	2.174 (5)	C(11)	C(16)	1.435 (5)
Ru	C(5)	2.165 (4)	C(12)	C(13)	1.402 (8)
Ru	C(6)	2.147 (9)	C(13)	C(14)	1.359 (9)
Ru	C(7)	2.161 (8)	C(14)	C(15)	1.409 (8)
Ru	C(8)	2.163 (6)	C(15)	C(16)	1.443 (9)
Ru	C(9)	2.168 (6)			

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
C(2)	C(1)	C(11)	127.4 (4)	C(12)	C(13)	C(14)	119.2 (6)
C(5)	C(1)	C(11)	125.9 (4)	C(13)	C(14)	C(15)	121.1 (5)
C(1)	C(11)	C(12)	119.4 (4)	C(14)	C(15)	C(14)	120.7 (6)
C(1)	C(11)	C(16)	120.8 (4)	C(14)	C(15)	C(16)	119.6 (3)
C(12)	C(11)	C(16)	119.5 (4)	C(11)	C(16)	C(11)	126.7 (5)
C(11)	C(12)	C(13)	122.2 (5)	C(11)	C(16)	C(15)	116.6 (3)

Table VII. Comparison of Distortions in 1a, 16, 1a⁺, and Related Peridisubstituted Naphthalenes

compd	rotatn of Cp from 90° orientatn ψ, deg	inter-Cp (or phenyl) ring angle θ, deg	av displacement of α,β-carbon atoms from naphthalene best plane, Å	displacement of ipso-Cp carbon atoms from naphthalene best plane, Å
1a	45.0 (1), 47.0 (1)	29.1 (1)	±0.170 (3), ±0.040 (3)	0.591 (3), −0.611 (3)
1b	42.0 (1)	26.2 (2)	±0.160 (4), ±0.037 (5)	±0.577 (4)
1a⁺	29.0 (2),ᵃ 31.8 (3)	17.5 (7)	±0.107 (6), ±0.009 (7)	+0.416 (6), −0.462 (6)
3	23		±0.015, ±0.005	
4	33	26	±0.044, ±0.010	
5	32	34	±0.091, ±0.048	

ᵃThis value is associated with the ferrocene moiety. **3**, 1,8-diphenylnaphthalene; **4**, 5,6-diphenylacenaphthene; **5**, 1,4,5,8-tetraphenylnaphthalene.
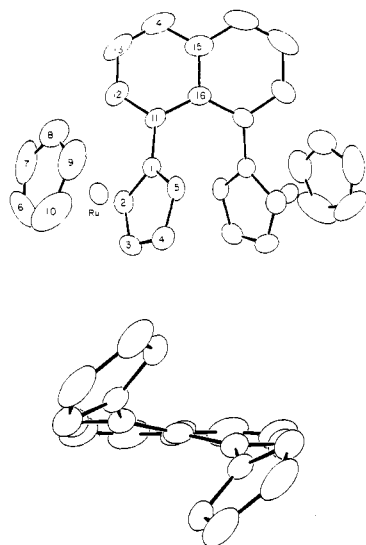

Figure 1. Molecular structure of **1b**, showing 50% probability ellipses. Lower drawing is a view parallel to the naphthalene plane, showing only the cyclopentadienyl rings bonded directly to the naphthalene moiety.
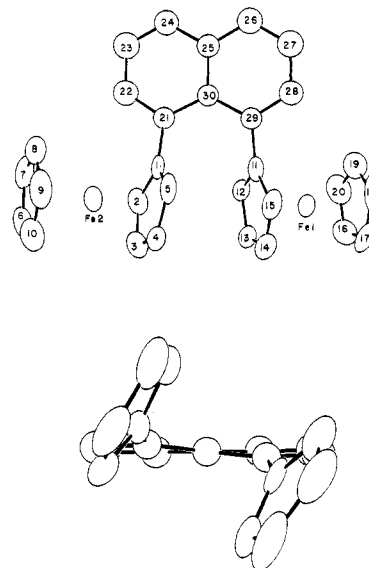

Figure 2. Views of the unit cell contents for **1a**, space group *P2₁/c*, and of **1b**, space group *C2/c*.

Figure 3. Molecular structure of **1a⁺**, showing 50% probability ellipses for atoms refined by using anisotropic temperature factors. Lower drawing is analogous to the lower drawing in Figure 1.
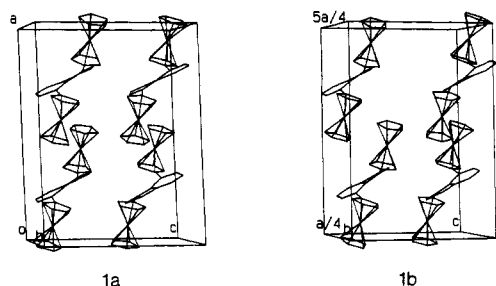
presented in Table VI. The views presented in Figure 1 are virtually identical with those[1] of the analogous Fe compound **1a**. As anticipated, the longer Cp–metal–Cp distance in **1b** of 3.63 Å, compared with 3.31 Å for Cp–Fe–Cp, leads to a decrease in the severity of the C(8)–C(12) contacts, which are 3.62 (1) Å in **1b** compared to 3.45 (1) Å in **1a**. Nevertheless, this has a relatively small impact on the magnitude of ψ, the rotation angle of the Cp group from an orientation perpendicular to the naphthalene plane. Significantly, this angle is only about 4° less in **1b** than it is in **1a**. Moreover, the dihedral angle θ between these rings is only about 3° less than it is in **1a** (Table VII). The near identity of the two structures is also reflected

Table VIII. Selected Bond Lengths (Å) and Angles (deg) for $[(C_{10}H_9Fe)_2C_{10}H_6]BF_4$

atom 1	atom 2	dist	atom 1	atom 2	dist
Fe(1)	C(11)	2.064 (5)	Fe(2)	C(8)	2.113 (6)
Fe(1)	C(12)	2.054 (5)	Fe(2)	C(9)	2.117 (7)
Fe(1)	C(13)	2.034 (6)	Fe(2)	C(10)	2.092 (7)
Fe(1)	C(14)	2.017 (7)	C(1)	C(21)	1.484 (9)
Fe(1)	C(15)	2.038 (6)	C(11)	C(29)	1.490 (9)
Fe(1)	C(16)	2.055 (7)	C(21)	C(22)	1.378 (7)
Fe(1)	C(17)	2.026 (6)	C(21)	C(30)	1.432 (8)
Fe(1)	C(18)	2.022 (7)	C(22)	C(23)	1.40 (1)
Fe(1)	C(19)	2.032 (7)	C(23)	C(24)	1.356 (9)
Fe(1)	C(20)	2.051 (7)	C(24)	C(25)	1.423 (7)
Fe(2)	C(1)	2.173 (6)	C(25)	C(26)	1.409 (9)
Fe(2)	C(2)	2.104 (7)	C(25)	C(30)	1.44 (1)
Fe(2)	C(3)	2.049 (6)	C(26)	C(27)	1.362 (8)
Fe(2)	C(4)	2.066 (5)	C(27)	C(28)	1.41 (1)
Fe(2)	C(5)	2.112 (5)	C(28)	C(29)	1.371 (9)
Fe(2)	C(6)	2.053 (6)	C(29)	C(30)	1.431 (6)
Fe(2)	C(7)	2.087 (6)			

| atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
C(2)	C(1)	C(21)	125.8 (6)	C(26)	C(25)	C(30)	120.5 (5)
C(5)	C(1)	C(21)	126.4 (6)	C(25)	C(26)	C(27)	119.9 (7)
C(1)	C(21)	C(22)	118.2 (5)	C(26)	C(27)	C(28)	120.3 (7)
C(1)	C(21)	C(30)	121.9 (4)	C(27)	C(28)	C(29)	121.7 (5)
C(22)	C(21)	C(30)	119.6 (6)	C(11)	C(29)	C(28)	118.8 (4)
C(21)	C(22)	C(23)	122.5 (6)	C(11)	C(29)	C(30)	121.5 (5)
C(22)	C(23)	C(24)	118.8 (5)	C(28)	C(29)	C(30)	119.5 (6)
C(23)	C(24)	C(25)	122.2 (7)	C(21)	C(30)	C(25)	117.7 (4)
C(24)	C(25)	C(26)	120.8 (6)	C(21)	C(30)	C(29)	125.0 (6)
C(24)	C(25)	C(30)	118.6 (6)	C(25)	C(30)	C(29)	117.3 (5)
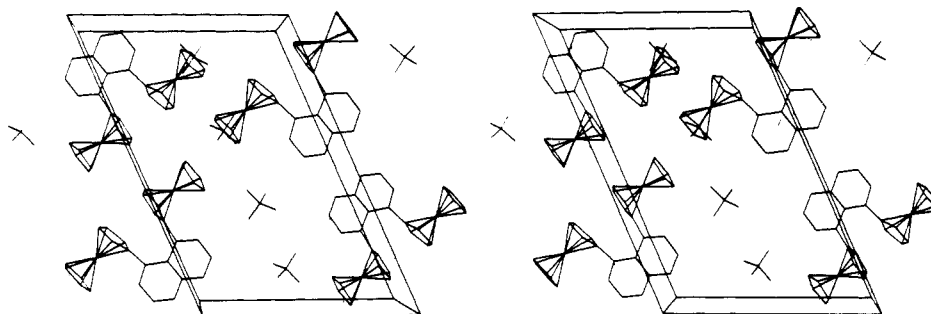
Figure 4. Stereoview of the unit cell contents for 1a⁺, projected down the crystallographic b axis. The a axis is horizontal, and c is vertical.

in the close correspondence of the average displacement of α- and β-carbon naphthalene atoms and of the ipso Cp carbon atom from the naphthalene best plane in these compounds. This is also shown in Table VII (full data are available as supplementary material). Inspection of the crystal structures of 1a and 1b (Figure 2) indicate that, although the space groups are different ($P2_1/c$ and $C2/c$), the packing arrangements are very similar. Furthermore, no unusually short intermolecular contacts are present in either crystal structure. These factors ensure the validity of the structural comparisons.

These results provide substantive evidence excluding the C(8)–C(12) contacts in 1a or 1b from contributing significantly to the much larger rotation angle ψ, which is found in these compounds, compared with the phenylated analogues 3, 4, and 5. The greater distortions in 1a,b may instead arise from charge repulsion between the cofacial cyclopentadienyl rings, since theoretical analyses have shown that there is significant charge accumulation on the cyclopentadienyl rings in ferrocene.[13] Furthermore, these

analyses show that removal of an electron from the highest filled E_{2g} level in ferrocene causes considerable charge depletion from the rings.

In order to examine this point further, we have carried out a crystal structure determination on 1a⁺, prepared by oxidation of 1a with 1 molar equiv of silver tetrafluoroborate. The structure of the molecular cation is shown in Figure 3, in views similar to those for 1b. Bond lengths and angles for the monocation, given in Table VIII, indicate that Fe1 (Fe–ring center, 1.716 (1), average Fe–C, 2.097 Å, cf.[14] 1.700 (2), 2.073 Å) is associated with the ferrocene nucleus and that Fe2 (Fe–ring center, 1.648 (1), average Fe–C, 2.039 Å, cf.[14] 1.656 (4), 2.018 Å) is associated with the ferricenium nucleus. Other bond lengths and angles lie in normal ranges. The most striking aspect of this structure, however, are the significantly smaller ψ angles and Cp dihedral angles compared with both these in 1a and 1b (Table VII). In 1a⁺, the Cp rings are rotated by an average of only 30.3° from the perpendicular orientation compared with 46° and 42° for 1a and 1b, respectively, while the dihedral angle between Cp ring pairs is ≈12° less than in 1a. In addition, the naphthalene ring is significantly less distorted from planarity (Table VII and supplementary material). The shortest C···C contacts to

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(14) Sullivan, B. W.; Foxman, B. M. *Organometallics* **1983**, *2*, 187.

the β-naphthalene carbon atoms are C8···C22 at 3.75(1) Å, C7···C22 at 3.80(1) Å, and C19···C28 at 3.45 (1) Å. It is of interest to note that the ferricenium cation is both *staggered* and *highly distorted*. The angle between the Cp ring planes is 9.1°, which is a very large distortion for a ferricenium cation.[14] The staggering and bending of the ferricenium cation occurs presumably to reduce the magnitude of the β-naphthalene–proton to Cp–proton nonbonded contacts. It is surprising, given the likely small barrier to ring rotation, that the staggering phenomenon does not occur in the neutral **1a** and **1b** species. As has been pointed out previously,[15] ferrocene usually occurs in a more nearly eclipsed rather than staggered conformation in properly analyzed structures, while unhindered ferricenium ions occur in the eclipsed conformation.[14,16] It is clear that a number of factors are responsible for the detailed distortions observed in these molecules. Nevertheless, the present results argue strongly that the primary contribution to the larger repulsion of cofacial aromatic rings in **1a** and **1b**, compared with the related phenylated naphthalenes **3**, **4**, and **5**, is the high negative charge on the Cp rings in the metallocenes, which is relieved by oxidation of one of the two metal centers.

The crystal structure of **1a⁺** is shown in Figure 4. Note that the cations occur in a distorted *stack* and are related

by the symmetry operation $(x, 1/2 - y, 1/2 + z)$ within the stack. The angle between pairs of intermolecular Cp rings in the stack is 26.6 (5)°. Representative C···C distances are C8···C18' at 3.30 (1) Å and C10···C17' at 3.47 (1) Å. However, although there are short contacts, no measurable conductivity was observed. It is quite possible that since the *b* axis is the direction of crystal elongation (this is the axis normal to the page in Figure 4), a remeasurement of conductivity along a more favorable direction is merited. Unfortunately, to date we have been unable to obtain crystals of sufficient size for such a measurement.

Supplementary Material Available: Tables SI through SVIII, listing thermal parameters, atomic coordinates for hydrogen atoms, additional bond lengths and angles, and best weighted least-squares planes for each structure (13 pages); tables of observed and calculated structure factors for each structure (17 pages). Ordering information is given on any current masthead page.

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One-Electron Oxidation of (η⁴-Cot)RhCp: Rearrangements of the Radical Cation and of the Resulting Dimerization Product[†]

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The complex (η⁴-Cot)RhCp (Cot = cyclooctatetraene; **3**) undergoes an irreversible one-electron oxidation to a transient radical cation. Detailed voltammetric studies suggest that the radical rearranges to (η⁵-C₈H₈)RhCp⁺ before dimerizing through the allyl radical section of the C₈ ring. Anodic or chemical oxidation (using [FeCp₂]⁺ or AgPF₆) in CH₂Cl₂ gives the C–C bonded dimer [(η⁵:η'⁵-C₁₆H₁₆)Rh₂Cp₂][PF₆]₂ (**4**) which thermally isomerizes to [(η²,η³:η'²,η'³-C₁₆H₁₆)Rh₂Cp₂][PF₆]₂ (**2b**) and then to [(η²,η³:σ',η'⁴-C₁₆H₁₆)Rh₂Cp₂][PF₆]₂ (**5**). The asymmetric species **5** has been fully characterized as the [BPh₄]⁻ salt by single-crystal X-ray diffraction. Crystallographic data: C₇₄H₆₆B₂Rh₂, *a* = 20.421 (5) Å, *b* = 15.198 (2) Å, *c* = 19.528 (4) Å, β = 114.10 (2)°, space group $P2_1/c$, *R* = 0.083, R_w = 0.077. The dication of **5** contains two rhodium atoms, each carrying an η⁵-cyclopentadienyl ring bridged [Rh···Rh = 6.514 (2) Å] by a C₁₆H₁₆ ligand. The ligand is formally derived from two Cot molecules by formation of three C–C bonds linking the two original C₈ rings. The resultant tetracyclic ligand bonds via σ,η⁴- and η²,η³-linkages to the two rhodium atoms, acting as a five-electron donor to each.

Introduction

With the exception of the reduction of [(η⁴-1,3-C₈H₈)-ML][ML = Fe(CO)₃[2] or CoCp[1,3]], one-electron oxidation or reduction of η⁴-bound cyclooctatetraene (Cot) complexes produces a structural rearrangement of the metal–π–sys-

tem. When the Cot ligand is bonded in a tub form through nonadjacent double bonds [e.g., as in (1,5-Cot)CoCp], the

†This may be considered as part 17 of the series Structural Consequences of Electron Transfer Reactions (part 16: Edwin, J., et al. *J. Am. Chem. Soc.*, 1987, *109*, 7893) and as part 28 of the series Reduction–Oxidation Properties of Organotransition-Metal Complexes (part 27: *J. Chem. Soc., Dalton Trans.*, in press).

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(1) Abbreviations used in this paper: C, chemical reaction following electron transfer (E); Cot, cyclooctatetraene; Cp, η⁵-cyclopentadienyl; CV, cyclic voltammetry; E_{pa}, anodic peak potential; FDMS, field desorption mass spectrum; RSD, relative standard deviation; SCE, saturated calomel electrode; TMS, tetramethylsilane; v, cyclic voltammetry scan rate.

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