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Synthesis, Characterization, and Electrochemical Studies of *β*,*β*′-Fused Metallocenoporphyrins

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β,β'-Fused monoruthenocenylporphyrins, Cp*Ru(III)[1,2-[M(II)-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)-porphyrinato]-3-methyl-cyclopentadienide] (M = Ni (**20**), Cu (**21**), Zn (**22**)), and bisferrocenoporphyrins, Fe(II) bis[1,2-[M(II)-5,10,15,20-tetraphenylporphyrinato]-3-methyl-cyclopentadienide] (M = Ni (**24**), Cu (**25**), Zn (**26**)), were synthesized and characterized. A novel synthetic approach to β,β'-fused porphyrins through Pd(0)-catalyzed [3 + 2] cycloaddition was implemented in this work. UV–vis spectra of these compounds show largely broadened and red-shifted bands (relative to their precursors) indicating potential electronic communication between the attached organometallic moiety and the porphyrin core. The electrochemistry of these molecules suggests significant electronic interactions between the metallocene and metalloporphyrin in molecules **20** and **24**. The crystal structure of the bisferrocenoporphyrin **26**, Fe(II) bis[1,2-[Zn(II)-5,10,15,20-tetraphenylporphyrinato]-3-methyl-cyclopentadienide], was determined: $\{Cp_2Fe[ZnTPP(THF)]_2\}\{Cp_2Fe[ZnTPP(THF)ZnTPP(MeOH)]\}\cdot 3MeOH\cdot 6THF$, $M = 3804.35$, monoclinic, space group $P2_1/c$, $a = 33.327(5)$ Å, $b = 19.145(3)$ Å, $c = 29.603(5)$ Å, $\beta = 106.309(2)°$, $V = 18128(5)$ Å^3, $Z = 4$. In this molecule, one porphyrin ring is rotated by about 72° with respect to the other in the 5-fold axis of the Cp ring.

Introduction

Molecular systems containing both porphyrin and metallocene fragments have been attracting significant attention over the past two decades as they show great potential in solar energy conversion,[1−6] small molecule activation,[7] molecular devices,[8−10] and porphyrin-assisted electron transfers.[11−13] Most of these applications hinge more or less on the effective interaction between the two fragments within one molecule. It is suggested that the communication between the two moieties depends on the type of spacer, relative spatial orientation, and distance between them. Numerous porphyrin systems appended with redox groups, such as ferrocene, have been prepared,[13−19] but effective communica-

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tion between them has been rarely observed. Recently, Burrell and co-workers[20] have reported the synthesis and studies of a series of functionalized porphyrins in which a porphyrin and an aryl group are connected with a conjugated link. Their investigation indicated that in certain cases communication between the functionality on the aryl group and the porphyrin core was apparent. Encouraged by the positive results, they prepared ferrocene-functionalized porphyrins[21] connecting in a similar fashion; unfortunately, their compounds failed to give evidence of strong interaction between the moieties. In a publication by Boyd and co-workers,[10] strong electronic metal−metal coupling between two remote ferrocenyl centers spaced by a porphyrin core was observed and supported by DFT calculations. Even though the precise factors leading to the strong coupling remained obscure, they suggested that the crowded substituents at porphyrin β-positions inhibit the rotation of the bulky *meso*-ferrocenyl moieties in such a way that extensive mixing of the molecular orbitals of the two systems results.

In most of the reported porphyrin−ferrocene systems, porphyrin and ferrocene are connected through various spacers at the porphyrin β- or *meso*-positions of the macrocycle. Direct connection through C−C single bond has only been reported for the *meso*-positions.[10,22−25] One can easily see that molecular orbitals of the two fragments in these molecules are not likely to overlap because of unfavorable alignment of the moieties within the molecule, arising partly from the bulkiness of the ferrocenyl group. We believe that to observe useful properties it is essential to design metallocene-appended porphyrin molecules with effective mixing of π-orbitals of the two systems. We decided to synthesize a series of metallocene−porphyrin conjugates, including monometallocenylporphyrins and bisporphyrinyl−metallocenes, in which the porphyrin and the metallocene fragments are directly fused to the porphyrin chromophore through β-positions. We assume that by "fusing" them in this way, the π-systems of each are "forced" to overlap and will thus enhance the interactions between them. One can envision that novel photo- and electrochemical properties will result from the fused molecules.

To attain the fused system, we explored a novel Pd(0)-catalyzed [3 + 2] cycloaddition reaction in the porphyrin series. This cycloaddition reaction effects tandem carbon−carbon bond formation on an electron-deficient double bond to generate a five-membered carbocycle in one step. In a previous communication[26] we briefly reported the synthesis and crystal structure of a fused monoruthenocenylporphyrin (Cp*Ru(III)[1,2-[Ni(II)-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)-porphyrinato]-3-methyl-cyclopentadienide) (Cp* = pentamethylcyclopentadienide) and a bisporphyrin ([Ni(II)-2,3-(β-methyl)propeno-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)-porphyrin]$_2$) as a byproduct. In the present paper, the synthesis of a series of monoruthenocenylporphyrins and bisporphyrinylferrocenes is detailed, the novel Pd(0)-catalyzed [3 + 2] cycloaddition reaction with activated porphyrins is investigated, and a new crystal structure of a bisporphyrinylferrocene (**26**) is reported. Electrochemical studies of these compounds indicate significant electronic communications within some of the molecules.

Experimental Section

Melting points (mp) were measured on a Thomas/Bristoline microscopic hot stage apparatus and were uncorrected. ^{1}H NMR spectra were obtained in deuterochloroform solution at 300 or 400 MHz using a Mercury 300 or Inova 400 spectrometer; chemical shifts are expressed in ppm relative to chloroform (7.26 ppm). Elemental analyses were performed at Midwest Microlabs., Inc., Indianapolis, IN. Electronic absorption spectra were measured using a Hitachi U-2000 spectrophotometer. Mass spectra (MALDI-TOF) were obtained at the Facility for Advanced Instrumentation, University of California, Davis.

Cyclic voltammetry was carried out using an EG&G Princeton Applied Research (PAR) 173 or 273 potentiostat/galvanostat. A homemade three-electrode cell was used for cyclic voltammetry and consisted of a platinum button or glassy carbon working electrode, a platinum counter electrode, and a homemade saturated calomel reference electrode (SCE). The SCE was separated from the bulk of the solution by a fritted glass bridge of low porosity that contained the solvent/supporting electrolyte mixture. Thin-layer UV−vis spectroelectrochemical experiments were performed with a home-built thin-layer cell which had a light-transparent platinum-net working electrode. Potentials were applied and monitored with an EG&G PAR model 173 potentiostat. Time-resolved UV−vis spectra were recorded with a Hewlett-Packard model 8453 diode array spectrophotometer.

All solvents and inorganic reagents were obtained from Fisher Scientific. All other chemicals were purchased from either Aldrich or Acros and were used without further purifications. Dichloromethane was distilled over $CaCl_2$; tetrahydrofuran was distilled over Na; N_2O_4 gas was prepared by reacting concentrated HNO_3 with zinc metal. Benzonitrile (PhCN) was obtained from Fluka or Aldrich Chemical Co. and was distilled over P_2O_5 under vacuum prior to use. Tetra-*n*-butylammonium perchlorate (TBAP) was purchased from Sigma Chemical or Fluka Chemika, recrystallized from ethyl alcohol, and dried under vacuum at 40 °C for at least one week prior to use.

X-ray diffraction measurements were carried out on a Bruker SMART 1000 with the use of Mo Kα radiation ($\lambda = 0.71073$ Å). Solution and refinement software used were SAINT for data reduction, SHELXS-97 for solution, and SHELXL97 for refinement. Due to the small crystal size and weak diffraction, the number of observed data was only 13 times the number of parameters when the Zn and Fe atoms were assigned anisotropic thermal parameters. Therefore, the remainder of the atoms were kept as isotropic.

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(26) {$Cp_2Fe[ZnTPP(THF)]_2$}{$Cp_2Fe[ZnTPP(THF)$ ZnTPP(MeOH)]}·3MeOH·6THF.

$C_{232}H_{211}Fe_{23}N_{16}O_{13}Zn_4$, **1**, $M = 3804.35$, monoclinic, $a = 33.327(5)$ Å, $b = 19.145(3)$ Å, $c = 29.603(5)$ Å, $\beta = 106.309(2)°$, $V = 18128(5)$ Å^3, space group $P2_1/c$, $Z = 4$, $T = 91(2)$ K, $D_{calcd} = 1.394$ Mg m^{-3}, μ(Mo Kα) = 0.749 mm^{-1}, 170 844 reflections measured, 26 022 unique ($R_{int} = 0.161$) used in all calculations. The final wR2 was 0.2470 (all data) and $R1(14\,016\ I > 2\sigma(I)) = 0.0906$, 1079 parameters. Residual electron density was 1.503 and −1.143 e Å^{-3}.

Synthesis

Nickel(II) 2,3-(β-Methylenepropano)-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)porphyrin (4). Strict air-free conditions and Schlenck techniques were used in the palladium(0)-catalyzed [3 + 2] coupling reactions. A mixture of 30 mg (0.13 mmol) of $Pd(OAc)_2$ and 200 μL (0.77 mmol) triisopropyl phosphite in 15 mL of THF was stirred at room temperature for 30 min. Measures of 1.17 g (1 mmol) of 2-nitroporphyrin **1** and 257 μL (1.3 mmol) of 2-[(trimethylsilyl)methyl]-2-propen-1-yl acetate were added. The reaction mixture was heated at 90 °C for 2 days and then at 100 °C for 2 days. The solvent was removed in vacuo, and the residue was purified by chromatography on silica gel (elution with CH_2Cl_2/cyclohexane ratio of 1:3), affording porphyrin **4** as red crystals (1 g, 85% yield): mp >300 °C; UV−vis (CH_2Cl_2), 404 nm (ϵ, 133 000), 532 (35 100), 568 (14 700); ^{1}H NMR ($CDCl_3$), δ, 8.86 ppm (d, ^3J (H,H) = 5.1 Hz, 2H), 8.81 (d, ^3J (H,H) = 5.1 Hz, 2H), 8.77 (s, 2H), 7.86 (d, ^4J (H,H) = 1.5 Hz, 4H), 7.7 (m, 8H), 4.95 (s, 2H), 3.41 (s, 4H), 1.46 (s, 36H), 1.44 (s, 36H); calcd for $C_{80}H_{96}N_4Ni$, 1172.3652; found MS (MALDI-TOF) *m/z* 1172.8. Anal. Calcd for $C_{80}H_{96}N_4Ni·2H_2O$: C, 79.55; H, 8.34; N, 4.63. Found: C; 79.15; H, 8.16; N, 4.75.

Nickel(II) 2,3-(β-Methylpropeno)-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)porphyrin (13). A mixture of 1.4 g (1.2 mmol) of **4** and 0.04 g (0.21 mmol) of *p*-TsOH in 30 mL of chloroform was heated at reflux for 24 h. It was cooled and then filtered to remove excess *p*-TsOH. The filtrate was washed with aqueous saturated Na_2CO_3 and then water. The solvent was then removed and the resulting residue was applied to a short silica gel plug and eluted with CH_2Cl_2/cyclohexane (v/v, 1:1). The first fraction was collected. The desired porphyrin **13** was recrystallized from CH_2Cl_2/MeOH to give red crystals (1.3 g, 93% yield): mp 285−286 °C; UV−vis (CH_2Cl_2), 416 nm (ϵ, 239 500), 540 (15 900), 581 (ϵ, 980); ^{1}H NMR ($CDCl_3$), δ, 8.84 ppm (d, ^3J (H,H) = 5.4 Hz, 1H), 8.82 (d, ^3J (H,H) = 5.2 Hz, 1H), 8.77 (overlapping d, ^3J (H,H) = 4.8 Hz, 2H), 8.73 (m, 2H), 7.84 (d, ^4J (H,H) = 1.6 Hz, 2H), 7.83 (d, ^4J (H,H) = 2.0 Hz, 2H), 7.71 (m, 3H), 7.66 (m, 3H), 5.46 (s, 1H), 3.00 (s, 2H), 2.03 (s, 3H), 1.42 (m, 72H); calcd for $C_{80}H_{96}N_4Ni$, 1172.3652; found MS (MALDI-TOF) *m/z* 1172.2. Anal. Calcd for $C_{80}H_{96}N_4Ni·CH_3OH·2H_2O$: C, 78.38; H, 8.45; N, 4.52. Found: C, 78.71; H, 9.00; N, 4.75.

Cp*ruthenium(III) [1,2-[Nickel(II)-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)porphyrinato]-3-methyl-cyclopentadienide] (20) and [Nickel(II) 2,3-(β-Methyl)propeno-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)porphyrin]$_2$ (23). Compound **13** (200 mg, 0.17 mmol) was dissolved in 15 mL of THF, and 350 μL of LDA (2 M in THF, 0.70 mmol) was added. The mixture was stirred at 0 °C under argon for 1 h. Cp*$RuCl_2$ (65 mg, 0.21 mmol) was added, and the resulting mixture was stirred at room temperature under strict air-free conditions for 2 days. The reaction mixture was then filtered through Celite to remove inorganic salts. The filtrate was evaporated to dryness. The residue was applied to a silica gel column, eluting with CH_2Cl_2/cyclohexane (v/v, 1:5). The second fraction was collected. This fraction was then subjected to size exclusion chromatography (Sephadex LH-20), eluting with THF. Two fractions were collected. *Fraction 1*: red crystals, **23**, 27 mg, 15% yield; UV−vis (CH_2Cl_2), λ_{max} 424 nm (ϵ, 105 000), 545 (ϵ, 15 900); ^{1}H NMR, δ, 8.95 ppm (br, 1H), 8.84 (d, ^3J (H,H) = 5.1 Hz, 1H), 8.75 (d, ^3J (H,H) = 4.5 Hz, 2H), 8.74 (d, ^3J (H,H) = 4.8 Hz, 2H), 8.67 (d, ^3J (H,H) = 5.1 Hz, 2H), 8.66 (d, ^3J (H,H) = 4.5 Hz, 2H), 8.57 (d, ^3J (H,H) = 4.8 Hz, 2H), 8.24 (br, 4H), 7.75 (t, ^4J (H,H) = 1.8 Hz, 2H), 7.72 (t, ^4J (H,H) = 1.8 Hz, 2H), 7.70 (t, ^4J (H,H) = 1.8 Hz, 2H), 7.69 (br, 2H), 7.50 (br, 4H), 7.26 (br, 4H), 6.58 (br, 4H), 6.43 (br, 4H), 5.09 (s, 2H)), 3.53 (s, 2H), 3.49 (s, 6H), 1.5−1.4 (m, 144H); calcd for $C_{160}H_{190}N_8Ni_2$, 2342.7146; found MS (MALDI-TOF) *m/z* 2338.6. Anal. Calcd for $C_{160}H_{190}N_8Ni_2$: C, 82.03; H, 8.17; N, 4.78. Found: C, 82.87; H, 8.88; N, 4.03. *Fraction 2*: recrystallized from CH_2Cl_2/MeOH as a green powder, **20**, 60 mg, 25% yield; mp >350 °C (dec); UV−vis (THF), λ_{max} 412 nm (ϵ, 103 000), 450 (77 000), 534 (18 100), 576 (16 100), 640 (18 500); ^{1}H NMR ($CDCl_3$), δ, 8.57 ppm (d, ^3J (H,H) = 4.8 Hz, 2H), 8.46 (s, 2H), 8.46 (d, ^3J (H,H) = 4.8 Hz, 2H), 7.80 (br, 8H), 7.66 (t, ^4J (H,H) = 1.8 Hz, 2H), 7.63 (t, ^4J (H,H) = 1.8 Hz, 2H), 3.88 (s, 2H), 1.74 (s, 3H), 1.43 (m, 72H), 0.89 (s, 15H); calcd for $C_{90}H_{110}N_4NiRu$, 1407.6558; found MS (MALDI-TOF) *m/z* 1408.0. Anal. Calcd for $C_{90}H_{110}N_4NiRu$: C, 76.79; H, 7.88; N, 3.98. Found: C, 77.05; H, 8.10; N, 3.82.

[Nickel(II) 2,3-(β-Methylpropeno)-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)porphyrin]$_2$ (23). Compound **13** (79 mg (0.067 mmol)) was dissolved in 5 mL of THF; 84 μL of LDA (2 M in THF, 0.17 mmol) was added at −78 °C under argon. The resulting mixture was stirred at 0 °C for 30 min and allowed to warm to room temperature for 30 min. The reaction mixture was then transferred to a solution of 11 mg (0.067 mmol) of $FeCl_3$ in 5 mL of THF under strict air-free conditions. The resulting mixture was heated to reflux for 2 days. It was cooled and then filtered through Celite to remove inorganic salts. The filtrate was evaporated to dryness under vacuum. The residue was then dissolved in 30 mL of CH_2Cl_2 and washed with 5% HCl and then water. The product was isolated on silica gel plates eluting with cyclohexane/CH_2Cl_2 (v/v, 6:1) as red crystals (12 mg, 15% yield) and was found to be spectroscopically identical with the material described above.

Nickel(II) 2,3-(β-Methylenepropano)-5,10,15,20-tetraphenylporphyrin (8). The title compound was prepared from Ni(II) 2-nitro-5,10,15,20-tetraphenylporphyrin (**6**) (0.85 g, 1.2 mmol) and 2-[(trimethylsilyl)methyl]-2-propen-1-yl acetate (0.36 mL, 1.8 mmol) using the procedure described for porphyrin **4**. It was obtained as red crystals in 83% yield: mp >300 °C; UV−vis (CH_2Cl_2), λ_{max} 414 nm (ϵ, 195 000), 527 (20 000), 612 (1300); ^{1}H NMR ($CDCl_3$), δ, 8.77 ppm (d, ^3J (H,H) = 5.1 Hz, 2H), 8.73 (d, ^3J (H,H) = 4.8 Hz, 2H), 8.73 (s, 2H), 8.00 (m, 4H), 7.86 (d, ^3J (H,H) = 7.8 Hz, 4H), 7.68 (m, 12H), 5.00 (s, 2H), 3.48 (s, 4H); calcd for $C_{48}H_{32}N_4Ni$, 723.5076; found MS (MALDI-TOF) *m/z* 722.8. Anal. Calcd for $C_{48}H_{32}N_4Ni·3H_2O$: C, 74.14; H, 4.92; N, 7.21. Found: C, 74.15; H, 4.84; N, 7.05.

Nickel(II) 2,3-(β-Methylpropeno)-5,10,15,20-tetraphenylporphyrin (11). The title compound was prepared from porphyrin **8** (0.66 g, 0.92 mmol) and *p*-TsOH (0.03 g, 0.16 mmol) using the procedure described for porphyrin **13** in 85% yield as red crystals: mp >300 °C; UV−vis (CH_2Cl_2), λ_{max} 416 nm (ϵ, 426 000), 534 (34 000); ^{1}H NMR ($CDCl_3$), δ, 8.74 ppm (m, 6H);7.89 (m, 8H), 7.66 (m, 12H), 5.57 (s, 1H), 3.09 (s, 2H), 2.10 (s, 3H); calcd for $C_{48}H_{32}N_4Ni$, 723.5076; found MS (MALDI-TOF) *m/z* 723.1. Anal. Calcd for $C_{48}H_{32}N_4Ni·2H_2O$: C, 75.83; H, 4.78; N, 7.37. Found: C, 75.50; H, 4.86; N, 7.15.

Iron(II) Bis[1,2-[Ni(II)-5,10,15,20-tetraphenylporphyrinato]-3-methyl-cyclopentadienide] (24). Compound **11** (0.21 g, 0.29 mmol) was dissolved in 25 mL of THF, and 0.36 mL of LDA (2 M in THF, 0.72 mmol) was added at 0 °C. The resulting mixture was stirred at 0 °C for 30 min and allowed to warm to room temperature for 30 min. $FeCl_2$ (6 mg, 0.44 mmol) was added under strict air-free conditions. The mixture was then heated at reflux for 2 days under argon. It was then cooled and filtered through Celite to remove inorganic salts. The filtrate was evaporated to dryness using a rotary evaporator. The residue was dissolved in 100 mL of CH_2Cl_2 and washed with 5% HCl and then water. The solvent was again removed. The residue was purified on a size-exclusion column (Sephadex LH-20), eluting with THF, to give the title compound as a dark brown powder (65 mg, 30% yield): mp >300 °C; UV−vis (THF), λ_{max} 416 nm (ϵ, 170 000), 530 (br); no well-defined Q bands were observed; ^{1}H NMR ($CDCl_3$), δ, 8.40 ppm (s, 4H), 8.01 (d, ^3J (H,H) = 4.8 Hz, 4H), 7.83 (d, ^3J (H,H) = 6.9 Hz, 8H), 7.70 (m, 16H), 7.44 (d, ^3J (H,H) = 4.8 Hz, 4H), 7.30 (br, 8H), 6.80 (br, 8H), 3.01 (s, 4H), 1.82 (s, 6H); calcd for $C_{96}H_{62}N_8FeNi_2$, 1500.8464; found MS (MALDI-TOF) *m*/*z* 1499.9.

Zinc(II) 2,3-(β-Methylene)-propano-5,10,15,20-tetraphenylporphyrin (18). The title compound was prepared from Zn(II) 2-nitro-5,10,15,20-tetraphenylporphyrin (0.2 g, 0.28 mmol) and 2-[(trimethylsilyl)methyl]-2-propen-1-yl acetate (0.072 mL, 0.36 mmol) using the procedure described for porphyrin **4** except a longer reaction time was employed (8 days). It was obtained in 2% yield as red crystals: mp >300 ^{o}C; UV−vis (CH_2Cl_2), λ_{max}, 412 nm (ϵ, 185 000), 525 (9600); ^{1}H NMR, δ, 3.6 ppm (s, 4H), 5.1 (s, 2H), 7.75 (m, 10H), 8.06 (overlapping d and s, ^4J (H,H) = 8.1 Hz, 4H), 8.22 (m, 6H), 8.82 (d, ^4J (H,H) = 4.8 Hz, 2H); 8.94 (d, ^4J (H,H) = 4.5 Hz, 2H), 8.93 (d, ^4J (H,H) = 4.8 Hz, 2H); calcd for $C_{48}H_{32}N_4Zn$, 730.1876; found MS (MALDI-TOF) *m*/*z* 729.4. Anal. Calcd for $C_{48}H_{32}N_4Zn\cdot CH_3OH$: C, 77.16; H, 4.76; N, 7.35. Found: C, 77.67; H, 5.08; N, 7.30.

Copper(II) 2,3-(β-Methylenepropano)-5,10,15,20-tetraphenylporphyrin (9). The title compound was prepared from Cu(II) 2-nitro-5,10,15,20-tetraphenylporphyrin (1.0 g, 1.39 mmol) and 2-[(trimethylsilyl)methyl]-2-propen-1-yl acetate (0.355 mL, 1.8 mmol) using the procedure described for porphyrin **4** in 80% yield as red crystals: mp >300 °C (dec); UV−vis (CH_2Cl_2), λ_{max}, 410 nm (ϵ, 385 000), 535 (22 000), 571 (1900); calcd for $C_{48}H_{32}N_4Cu$, 728.3536; found MS (MALDI-TOF) *m*/*z* 727.9. Anal. Calcd for $C_{48}H_{32}N_4Cu\cdot 0.5CH_3OH$: C, 78.22; H, 4.61; N, 7.52. Found: C, 79.22; H, 5.72; N, 7.05.

Copper(II) 2,3-(β-Methylpropeno)-5,10,15,20-tetraphenylporphyrin (12). The title compound was prepared from porphyrin **9** (0.45 g, 0.62 mmol) and *p*-TsOH (0.03 g, 0.16 mmol) using the procedure described for porphyrin **11** in 90% yield as red crystals: mp >350 °C (dec); UV−vis (CH_2Cl_2), λ_{max}, 411 nm (ϵ, 323 000), 540 (22 900); calcd for $C_{48}H_{32}N_4Cu$, 728.3536; found MS (MALDI-TOF) *m*/*z* 727.6. Anal. Calcd for $C_{48}H_{32}N_4Cu\cdot H_2O\cdot 0.5CH_3OH$: C, 78.19; H, 4.61; N, 7.52. Found: C, 78.70; H, 5.68; N, 7.01.

Iron(II) Bis[1,2-[copper(II)-5,10,15,20-tetraphenylporphyrinato]-3-methyl-cyclopentadienide] (25). The title compound was prepared from compound **12** (0.27 g, 0.37 mmol), LDA (2 M in THF, 0.93 mmol), and $FeCl_2$ (0.094 g, 0.74 mmol) using the procedure described for **27** in 8% yield as a brown powder: mp >300 °C; UV−vis (CH_2Cl_2), λ_{max}, 410 nm (ϵ, 132 000), no well-defined Q bands; calcd for $C_{96}H_{62}N_8FeNi_2$,1510.5384; found MS (MALDI-TOF) *m*/*z* 1508.9.

2,3-(β-Methylenepropano)-5,10,15,20-tetraphenylporphyrin (15) and 2,3-(β-Methylpropeno)-5,10,15,20-tetraphenylporphyrin (16). Compound **9** (0.5 g) was mixed with 1 mL of H_2SO_4 and 20 mL of TFA. This mixture was stirred at room temperature for 15 min. Saturated aqueous Na_2CO_3 was carefully added to neutralize the acids. After being stirred at room temperature for 10 min, this mixture was extracted with CH_2Cl_2. The organic layer was separated and washed with aqueous $NaHCO_3$ and then water. The solvent was removed using a rotary evaporator. The product (a mixture of **16** and **15**) was crystallized from CH_2Cl_2/MeOH to give 0.4 g (90% yield). This material (80 mg) was then treated with 10 mg of *p*-TsOH in chloroform under reflux temperature for 1 day; pure **16** was obtained as red crystals after chromatography (Al_2O_3, eluted with CH_2Cl_2) and recrystallization (CH_2Cl_2/MeOH) (70 mg, 88% yield): mp >300 °C (dec); UV−vis, λ_{max} 424 nm (ϵ, 182 000), 520 (14 500), 553 (7900), 593 (5900), 647 (4900); ^{1}H NMR, δ, 8.87 ppm (overlapping d, 2H), 8.77 (overlapping d, 2H), 8.74 (d, ^3J (H,H) = 5.1 Hz, 1H), 8.70 (d, ^3J (H,H) = 5.1 Hz, 1H), 8.22 (m, 4H), 8.15 (dd, ^3J (H,H) = 8.4 Hz, ^4J (H,H) = 1.8 Hz, 2H), 8.08 (dd, ^3J (H,H) = 8.4 Hz, ^4J (H,H) = 2.1 Hz, 2H), 7.75 (m, 12H), 5.78 (s, 1H), 3.30 (s, 2H), 2.22 (s, 3H), −2.89 (br, 2H); calcd for $C_{48}H_{34}N_4$, 666.8234; found MS (MALDI-TOF) *m*/*z* 670.2. Anal. Calcd for $C_{48}H_{34}N_4\cdot 3H_2O$: C, 79.96; H, 5.59; N, 7.77. Found: C, 79.55; H, 5.83; N, 7.27.

Zinc(II) 2, 3-(β-Methylpropeno)-5,10,15,20-tetraphenylporphyrin (17). Compound **16** (0.32 g, 0.48 mmol) was dissolved in 60 mL of CH_2Cl_2, and 1.3 g (5.9 mmol) of $Zn(OAc)_2$ in 20 mL of MeOH was added. This mixture was stirred at room temperature for 1 day and then filtered through Celite to remove excess $Zn(OAc)_2$. The solvent was removed. The residue was applied to a short alumina plug, eluting with CH_2Cl_2. The first fraction was collected. The solvent was again removed. The product was recrystallized from CH_2Cl_2/MeOH to give the title compound as purple crystals (0.26 g, 74% yield): mp >300 °C (dec); UV−vis (CH_2Cl_2), λ_{max}, 418 nm (ϵ, 249 000), 515 (4100), 551 (12 400), 606 (11 600), 697 (3900); ^{1}H NMR, δ, 8.94 ppm (overlapping d, 4H), 8.89 (d, ^3J (H,H) = 5.0 Hz, 1H), 8.84 (d, ^3J (H,H) = 5.0 Hz, 1H), 8.22 (m, 4H), 8.15 (dd, ^3J (H,H) = 8.0 Hz, ^4J (H,H) = 1.5 Hz, 2H), 8.09 (dd, ^3J (H,H) = 7.8 Hz, ^4J (H,H) = 1.5 Hz, 2H), 7.74 (m, 12H), 5.70 (s, 1H), 3.2 (s, 2H), 2.2 (s, 3H); calcd for $C_{48}H_{32}N_4Zn$, 730.1876; found MS (MALDI-TOF) *m*/*z* 729.1. Anal. Calcd for $C_{48}H_{32}N_4Zn$: C, 78.96; H, 4.42; N, 7.67. Found: C, 78.89; H, 4.78; N, 7.71.

Iron(II) Bis[1,2-[zinc(II)-5,10,15,20-tetraphenylporphyrinato]-3-methyl-cyclopentadienide] (26). The title compound was prepared from compound **17** (190 mg, 0.26 mmol), LDA (2 M in THF, 0.65 mmol), and $FeCl_2$ (66 mg, 0.52 mmol) using the procedure described for compound **24** in 35% yield as purple crystals: mp >300 °C; UV−vis ($CHCl_3$), λ_{max}, 412 nm (ϵ, 200 000), 520 (15 900), 553 (8600), 629 (7200); ^{1}H NMR ($CDCl_3$), δ, 8.62 ppm (s, 4H), 8.29 (d, ^3J (H,H) = 4.5 Hz, 4H), 8.21(br, 6H), 7.92 (d, ^3J (H,H) = 7.5 Hz, 4H), 7.76 (br, 8H), 7.63 (rb, 6H), 7.26 (m, 16H), 7.09 (d, ^3J (H,H) = 7.2 Hz, 6H), 6.10 (br, 4H), 5.41 (br, 4H), 3.28 (s, 4H), 2.02 (s, 6H); calcd for $C_{96}H_{62}N_8FeZn_2$, 1514.2064; found MS (MALDI-TOF) *m*/*z* 1512.2.

Copper(II) 2-Nitro-5,10,15,20-tetrakis(3,5-di-*tert*-butyl)phenylporphyrin (5). The title compound was prepared from Cu(II) 5,10,15,20-tetrakis(3,5-di-*tert*-butyl)phenylporphyrin (**35**) (1.2 g, 1.07 mmol) and freshly made N_2O_4 gas, in 89% yield, as purple crystals: mp >300 °C (dec); UV−vis (CH_2Cl_2), λ_{ma}, 425 nm (ϵ, 130 000), 549 (9000), 590 (5700); calcd for $C_{76}H_{91}CuN_5O$, 1170.1132; found MS (MALDI-TOF) *m*/*z* 1169.6. Anal. Calcd for $C_{76}H_{91}CuN_5O\cdot 2H_2O$: C, 75.93; H, 7.82; N, 5.83. Found: C, 75.74; H, 7.77; N, 5.89.

Copper(II) 2,3-(β-Methylenepropano)-5,10,15,20-tetrakis(di-*tert*-butyl-phenyl)porphyrin (10). The title compound was prepared from compound **5** (1.1 g, 0.94 mmol) and 2-[(trimethylsilyl)-methyl]-2-propen-1-yl acetate (0.24 mL, 1.22 mmol) using the procedure described for porphyrin **4** in 87% (1.0 g) yield as red crystals: mp >300 °C (dec); UV−vis (CH_2Cl_2), λ_{max} 416 nm (ϵ, 242 000), 549 (14 100), 570 (1400); calcd for $C_{80}H_{96}CuN_4$, 1177.2112; found MS (MALDI-TOF) *m/z* 1175.9. Anal. Calcd for $C_{80}H_{96}Cu\ N_4O{\cdot}C_4H_8O$: C, 81.04; H, 8.42; N, 4.50. Found: C, 81.34; H, 9.28; N, 4.39.

Copper(II) 2,3-(β-Methylpropeno)-5,10,15,20-tetrakis(di-*tert*-butyl-phenyl)porphyrin (14). The title compound was prepared from porphyrin **10** (0.15 g, 0.12 mmol) and *p*-TsOH (0.01 g, 0.05 mmol) using the procedure described for porphyrin **13** in 80% (0.12 g) yield as red crystals: mp >350 °C; UV−vis (CH_2Cl_2), λ_{max} 418 nm (ϵ, 275 000), 544 (18 600); calcd for $C_{80}H_{96}Cu\ N_4$, 1177.2112; found MS (MALDI-TOF) *m/z* 1176.2. Anal. Calcd for $C_{80}H_{96}CuN_4O{\cdot}0.5CH_3OH$: C, 81.03; H, 8.28; N, 4.69. Found: C, 81.07; H, 9.19; N, 4.56.

Cp*ruthenium(II) [1,2-[Copper(II)-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)porphyrinato]-3-methyl-cyclopentadienide] (21). The title compound was prepared from porphyrin **14** (0.12 g, 0.10 mmol), LDA (2 M in THF, 0.25 mmol), and Cp*$RuCl_2$ (0.062 g, 0.20 mmol) using the procedure described for porphyrin **20** in 14% (20 mg) yield as a brownish-green powder: mp >300 °C; UV−vis (CH_2Cl_2), λ_{max}, 423 nm (ϵ, 106 000), 548 (5600); calcd for $C_{90}H_{110}CuN_4Ru$, 1412.5018; found MS (MALDI-TOF) *m/z* 1412.0. Anal. Calcd for $C_{90}H_{110}Cu\ N_4Ru{\cdot}2H_2O$: C, 74.65; H, 7.93; N, 3.87. Found: C, 74.53; H, 8.56; N, 4.29.

2,3-(β-Methylenepropano)-5,10,15,20-tetrakis(3,5-di-*tert*-butyl)phenylporphyrin (36) and 2,3-β-(Methylpropeno)-5,10,15,-20-tetrakis(3,5-di-*tert*-butyl)porphyrin (37). Compound **10** (0.65 g, 0.55 mmol) was treated with 27.5 mL of 10% (v/v) H_2SO_4 in TFA for 10 min at room temperature. To this mixture was added 25 mL of water and 50 mL of CH_2Cl_2. The organic layer was separated and washed with saturated aqueous Na_2CO_3 and then water. The solvent was removed using a rotary evaporator. The residue was passed through a short alumina plug, eluting with CH_2Cl_2. The mixture of **36** and **37** was crystallized from CH_2Cl_2/MeOH as purple crystals: calcd for $C_{80}H_{98}N_4$, 1115.681; found MS (MALDI-TOF) *m/z* 1114.3. Anal. Calcd for $C_{80}H_{98}N_4{\cdot}CH_3OH$: C, 84.87; H, 8.97; N, 4.89. Found: C, 84.84; H, 8.71; N, 5.03.

2,3-(β-Methylpropeno)-5,10,15,20-tetrakis(3,5-di-*tert*-butyl)-porphyrin (37). The title compound was prepared from a mixture of **36** and **37** (0.4 g, 0.36 mmol) and *p*-TsOH (0.01 g, 0.05 mmol) using the procedure described for porphyrin **16** in 88% (0.35 g) yield as red crystals: mp >300 °C; UV−vis (CH_2Cl_2), λ_{max} 427 nm (ϵ, 218 000), 523 (10 400), 551 (3100), 594 (600), 648 (2500); ^{1}H NMR, δ, 8.94 ppm (br, 2H), 8.83 (br, 2H), 8.82 (d, ^3J (H,H) = 5.4 Hz, 1H), 8.75 (d, ^3J (H,H) = 5.4 Hz, 1H), 8.09 (mixture of two d, ^4J (H,H) = 2.0 Hz, ^4J (H H) = 2.0 Hz, 4H), 8.03 (d, ^4J (H,H) = 1.8 Hz, 2H), 7.94 (d, ^4J (H,H) = 1.8 Hz, 2H), 7.83 (m, 2H), 7.77 (m, 2H), 5.73 (s, 1H), 3.24 (s, 2H), 2.17 (s, 3H), 1.54 (br, 72H), −2.85 (br, 2H); calcd for $C_{80}H_{98}N_4$, 1115.681; found MS (MALDI-TOF) *m/z* 1114.3. Anal. Calcd for $C_{80}H_{98}N_4$: C, 86.13; H, 8.85; N, 5.02. Found: C, 85.84; H, 8.96; N, 5.11.

Zinc(II) 2,3-(β-Methylpropeno)-5,10,15,20-tetrakis(3,5-di-*tert*-butyl)porphyrin (19). Compound **37** (0.13 g, 0.12 mmol) was dissolved in 15 mL of $CHCl_3$, and 0.27 g (1.2 mmol) of $Zn(OAc)_2$ in 5 mL of MeOH was added. Argon was bubbled through this mixture for 5 min. It was then stirred at room temperature under argon, overnight. The solvent was removed using a rotary evaporator. The residue was applied to a short alumina plug, eluting with cyclohexane/CH_2Cl_2 (v/v, 2:1). The first red fraction was collected. The desired compound was recrystallized from CH_2Cl_2/MeOH (0.1 g, 73% yield): mp >300 °C; UV−vis (CH_2Cl_2), λ_{max}, 420 nm (ϵ, 130 000), 559 (3500) 608 (9100), 697 (3800); ^{1}H NMR, δ, 8.97 ppm (mixture of two d, 5H), 8.87 (d, ^3J (H,H) = 4.8 Hz 1H), 8.08 (t, ^4J (H,H) = 1.6 Hz, 4H), 8.01 (d, ^4J (H,H) = 2.0 Hz, 2H), 7.92 (d, ^4J (H,H) = 2.0 Hz, 2H), 7.81 (m, 2H), 7.75 (m, 2H), 5.62 (s, 1H), 3.17 (s, 2H), 2.12 (s, 3H); calcd for $C_{80}H_{96}N_4Zn$, 1179.0452; found MS (MALDI-TOF) *m/z* 1180.9. Anal. Calcd for $C_{80}H_{96}N_4Zn{\cdot}CH_3OH$: C, 80.26; H, 8.32; N, 4.62. Found: C, 80.45; H, 8.15; N, 4.64.

Cp*ruthenium(II) [1,2-[Zinc(II)-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)-porphyrinato]-3-methyl-cyclopentadienide] (22). The title compound was prepared from **19** (70 mg, 0.059 mmol), LDA (2 M in THF, 0.15 mmol), and Cp*Ru(III)Cl_2 (0.038 g, 0.12 mmol) using the procedure described for **20** in 2% (2 mg) yield. MS (MALDI-TOF) *m/z* 1414.9. Further characterization was not possible due to instability.

Nickel(II) 2,3-(β-Methylenepropano)-7-nitro-5,10,15,20-tetrakis(di-*tert*-butyl-phenyl)porphyrin, Nickel(II) 2,3-(β-Methylenepropano)-8-nitro-5,10,15,20-tetrakis(di-*tert*-butyl-phenyl)-porphyrin, and Nickel(II) 2,3-(β-Methylenepropano)-17-nitro-5,10,15,20-tetrakis(di-*tert*-butyl-phenyl)porphyrin. The mixture of the title compounds was prepared from Ni(II) 5,10,15,20-tetrakis-(3,5-di-*tert*-butyl)phenylporphyrin (**4**) (0.65 g, 0.55 mmol) and freshly made N_2O_4 gas using the procedure described for compound **1** in 89% (0.6 g) yield. This mixture was not further separated and was used directly in the following step.

Nickel(II) 2,3;17,18-Bis(β-methylenepropano)-5,10,15,20-tetrakis(di-*tert*-butyl-phenyl)porphyrin (27) and Nickel(II) 2,3;7,8-Bis(β-methylenepropano)-5,10,15,20-tetrakis(di-*tert*-butyl-phenyl)-porphyrin (28).

The title compounds were prepared from the preceding mixture (0.5 g, 0.4 mmol) and 2-[(trimethylsilyl)methyl]-2-propen-1-yl acetate (0.20 mL, 1.02 mmol) using the procedure described for porphyrin **4** as a mixture of **27** and **28** that was separated on silica gel plates, eluting with cyclohexane/CH_2Cl_2 (v/v, 15:1). Yields: **27**, 50 mg; **28**, 50 mg. *Compound **27***: mp >300 °C; UV−vis, λ_{max} 416 nm (ϵ, 219 000), 528 (12 500); ^{1}H NMR, δ, 8.87 ppm (s, 4H), 7.8 (m, 12H), 4.93 (s, 4H), 3.39 (s, 8H), 1.4 (s, 72H); calcd for $C_{84}H_{100}N_4Ni$, 1224.4408; found MS (MALDI-TOF) *m/z* 1223.3. Anal. Calcd for $C_{84}H_{100}N_4Ni{\cdot}0.5H_2O$: C, 81.80; H, 8.25; N, 4.54. Found: C, 81.97; H, 8.37; N, 4.71. *Compound **28***: mp >300 ^{o}C; UV−vis, λ_{max} 413 nm (ϵ, 203 000), 527 (20 000); calcd for $C_{84}H_{100}N_4Ni$, 1224.4408; found MS (MALDI-TOF) *m/z* 1223.2.

Nickel(II) 2,3;17,18-Bis(β-methylpropeno)-5,10,15,20-tetrakis-(3,5-di-*tert*-butyl)porphyrin (29)/(30). The title compounds were prepared as a mixture from porphyrin **27** (0.1 g, 0.08 mmol) and *p*-TsOH (0.01 g, 0.05 mmol) using the procedure described for porphyrin **13** in 80% yield as a mixture of two isomeric compounds. This mixture was not further separated and was used directly in the bisruthenocenoporphyrin-forming reaction. Calcd for $C_{84}H_{100}N_4Ni$: 1224.4408; found MS (MALDI-TOF) *m/z* 1224.1.

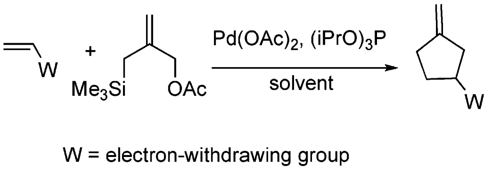
Nickel(II) 2,3-(β-Oxopropano)-5,10,15,20-tetraphenylporphyrin (33). Compound **8** (0.3 g, 0.41 mmol) was dissolved in 60 mL of THF and 20 mL of dioxane. $NaIO_4$ (0.66 g) in 6 mL of water was added. Argon was bubbled through the solution for 5 min. OsO_4 (30 mg) was then added. The resulting mixture was stirred at room temperature under argon for 4 h. It was then filtered through Celite to remove inorganic salts. The filtrate was evaporated to dryness, and the residue thus obtained was redissolved in 100 mL of CH_2Cl_2 and washed with water. The solvent was then removed under reduced pressure. The residue was subjected to a silica gel column, eluted with CH_2Cl_2. Two fractions were collected. The first fraction was unreacted starting material (10 mg); the second fraction was the desired porphyrin **33** (0.15 g, 50% yield): mp >300 °C; UV−vis, λ_{max} 414 nm (ϵ, 317 000), 527 (18 100); ^{1}H NMR, δ, 8.77 ppm (d, ^3J (H,H) = 5.2 Hz 2H), 8.73 (s, 2H), 8.73 (d, ^3J (H,H) = 5.2 Hz, 2H), 7.97 (dd, ^3J (H,H) = 7.8 Hz, ^4J (H,H) = 1.8 Hz, 4H), 7.83 (dd, ^3J (H,H) = 5.2 Hz, ^4J (H,H) = 1.6 Hz, 4H), 7.65 (m, 12H), 3.33 (s, 4H); calcd for $C_{47}H_{30}N_4NiO$, 725.4802; found MS (MALDI-TOF) *m*/*z* 725.9. Anal. Calcd for $C_{47}H_{30}N_4NiO\cdot H_2O$: C, 75.93; H, 4.34; N, 7.54. Found: C, 76.35; H, 4.43; N, 7.52.

Nickel(II) 2,3-(β-Hydroxypropano)-5,10,15,20-tetraphenylporphyrin (34). $TiCl_3(DME)_{1.5}$ (50 mg, 0.17 mmol) (DME = dimethoxyethane) and 46 mg of Zn−Cu couple were mixed in 15 mL of THF. Argon was bubbled through this mixture for 5 min. It was then heated under reflux for 2.5 h. The reaction mixture was cooled, and 50 mg (0.069 mmol) of **33** in 5 mL of THF containing one drop of pyridine was added. Argon was again bubbled through this mixture for 5 min. The mixture was then heated under reflux overnight before being cooled and then filtered through Celite to remove inorganic salts. The filtrate was evaporated to dryness. The residue was dissolved in CH_2Cl_2 and washed with 5% HCl and then water. After re-evaporation of the solvent, the residue was subjected to a short silica gel plug, eluting with cyclohexane/CH_2Cl_2 (v/v, 2:1). The second fraction was collected. Compound **34** was recrystallized from CH_2Cl_2/MeOH as red crystals (20 mg, 40% yield): mp >300 °C; UV−vis, λ_{max} 414 nm (ϵ, 496 000), 527 (45 000); ^{1}H NMR, δ, 8.78 ppm (d, ^3J (H,H) = 5.2 Hz, 2H), 8.74 (s, 2H), 8.73 (d, ^3J (H,H) = 5.2 Hz, 2H), 8.00 (dd, ^3J (H,H) = 8.0 Hz, ^4J (H,H) = 1.2 Hz, 4H), 7.86 (br, 4H), 7.7 (m, 12H), 4.89 (m, 1H), 3.2 (dd, ^2J (H,H) = 16.4 Hz, ^3J (H,H) = 6.4 Hz, 2H), 2.6 (dd, ^2J (H,H) = 16.4 Hz, ^3J (H,H) = 3.0 Hz, 2H); calcd for $C_{47}H_{32}N_4NiO$, 727.496; found MS (MALDI-TOF) *m*/*z* 727.09. Anal. Calcd for $C_{47}H_{32}N_4NiO\cdot H_2O$: C, 75.65; H, 4.60; N, 7.51. Found: C, 75.60; H, 4.28; N, 7.54.

Results and Discussions

Synthesis. Porphyrin macrocycles possess 22 π-electrons, but only 18 of them are involved in any specific delocalization pathway. Upon peripheral annelation, one or even two 6 π-electron cyclopentadienide anions can be added to form 26 or 30 π-electron systems that still maintain the aromatic stability of the porphyrin chromophore. Examples of metallocenes prepared from cyclopentadienide ions containing condensed aromatic rings have been described.[27−30] Those studies suggest that annelation or "fusion" does not necessarily cause the electrons to become less available to the cyclopentadienide ion. However, the fact that porphyrins can act as a π-ligand to transition metals either through one pyrrolic[31] ring or through the porphyrin core[32] leads to reactivity uncertainties; for example, once prepared, would the anion from the fused cyclopentadiene ring be localized to the five-membered ring or diffusely delocalized over the whole porphyrin macrocycle? This stimulated us to investigate how the two moieties would fuse together and how reactive the whole system might be.

Scheme 1



Pd(0)-Catalyzed [3 + 2] Cycloaddition Reaction on 2-Nitroporphyrins. To introduce a fused five-membered ring into the porphyrin periphery as the precursor of Cp^-, we investigated a [3 + 2] cycloaddition reaction catalyzed by Pd(0) (Scheme 1). This cycloaddition produces a five-membered ring bearing an exo-double bond function, simplifying the subsequent transformation to afford a methylcyclopentadienide ion.

This type of cycloaddition reaction has been described before for isolated activated double bonds.[33−36] An electron-deficient double bond and an in situ generated 1,3-dipole are required for the reaction to occur. Strongly electron-withdrawing groups, such as ester, nitrile, nitro, ketone, and sulfone, are deemed necessary to activate the double bonds. To apply this chemistry to a porphyrin, we chose 2-nitro-5,10,15,20-tetraarylporphyrins because these porphyrins are readily prepared by scalable, chromatography-free procedures and possess a unique set of reactivities that facilitate peripheral functionalization.[37−39] 2-Nitro-5,10,15,20-tetraphenylporphyrin has been shown to undergo nucleophilic attack at the β,β′ double bond bearing the nitro group, leading to a range of β-substituted porphyrins. The strong ability of the nitro group to activate a *meso*-tetraarylporphyrin toward [3 + 2] cycloaddition and its propensity to act as leaving group were also demonstrated in the related syntheses of pyrroloporphyrins.[39]

Ni(II) 2-nitro-5,10,15,20-tetrakis-(3,5-di-*tert*-butyl)phenylporphyrin (**1**) (Scheme 2) was prepared by nitration of Ni(II) porphyrin **2** with N_2O_4[39] in CH_2Cl_2. Metalation of free base porphyrin **3** is necessary to avoid insertion of Pd into the porphyrin core in the subsequent step. The Pd(0) catalyst was prepared[40] in situ by treatment of $Pd(OAc)_2$ with triisopropylphosphite at room temperature for 30 min under strictly air-free conditions. To this freshly made Pd(0) catalyst was added nitroporphyrin **1** and 2-[(trimethylsilyl)methyl]-2-propen-1-yl acetate, with exclusion of air. This mixture was placed in a preheated (90 °C) oil bath for 2 days.

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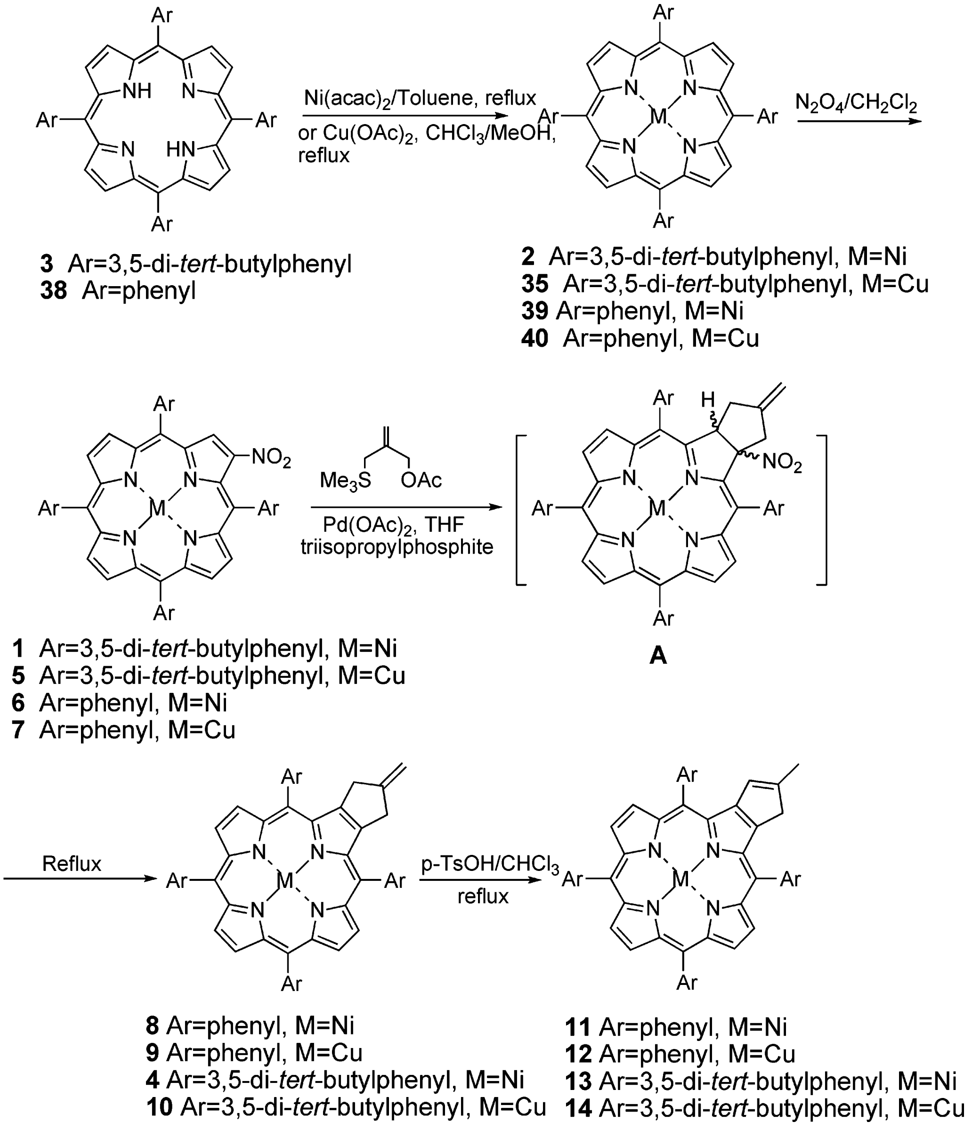
Scheme 2



3 Ar=3,5-di-*tert*-butylphenyl
38 Ar=phenyl

2 Ar=3,5-di-*tert*-butylphenyl, M=Ni
35 Ar=3,5-di-*tert*-butylphenyl, M=Cu
39 Ar=phenyl, M=Ni
40 Ar=phenyl, M=Cu

1 Ar=3,5-di-*tert*-butylphenyl, M=Ni
5 Ar=3,5-di-*tert*-butylphenyl, M=Cu
6 Ar=phenyl, M=Ni
7 Ar=phenyl, M=Cu

A

8 Ar=phenyl, M=Ni
9 Ar=phenyl, M=Cu
4 Ar=3,5-di-*tert*-butylphenyl, M=Ni
10 Ar=3,5-di-*tert*-butylphenyl, M=Cu

11 Ar=phenyl, M=Ni
12 Ar=phenyl, M=Cu
13 Ar=3,5-di-*tert*-butylphenyl, M=Ni
14 Ar=3,5-di-*tert*-butylphenyl, M=Cu

Reaction progress was monitored using TLC and indicated formation of a single new green compound. ^{1}H NMR and MS (MALDI-TOF) spectra of the isolated product revealed that it was a complex mixture. Fortunately, it was noticed later that the green spot on TLC later turned red. It seemed that the green spot, which was believed to be an isomeric mixture of nitrochlorin **A**, was not stable. The loss of the nitro group occurred upon exposure to silica gel. This mixture was then mixed with silica gel in THF at 90 °C for 2 days, and pure porphyrin **4** was obtained. The appearance of two new sets of chemical shifts at 4.9 (s, 2H) and 3.4 ppm (s, 4H) in the ^{1}H NMR spectrum confirmed the successful synthesis of propanoporphyrin **4**. Porphyrin **4** could also be obtained directly from the [3 + 2] cycloaddition reaction in one-pot synthesis via prolonged heating at a higher temperature (100 °C). This reaction was clean and high yielding (up to 88%).

Similar reactions carried out with Cu(II) 2-nitro-5,10,15,-20-tetrakis-di-*tert*-butylphenylporphyrin (**5**), Ni(II) 2-nitro-5,10,15,20-tetraphenylporphyrin (**6**), and Cu(II) 2-nitro-5,10,15,20-tetraphenylporphyrin (**7**) were also successful, giving ~80% yields. However, the [3 + 2] cycloaddition reaction with Zn(II) 2-nitro-5,10,15,20-tetraphenylporphyrin (prepared by nitration of free base TPP with ZnNO$_2$ followed by insertion of Zn(II)) required higher temperature and longer reaction time and afforded a very low yield of the desired porphyrin **18** (no more than 5% yield). This suggests that Zn(II) porphyrins are less activated toward this [3 + 2] cycloaddition, possibly because of the greater electron back-donating ability of Zn(II) (d^{10}) relative to Ni(II) (d^8) and Cu(II) (d^9).

Fused Cyclopentadienylporphyrins: The Precursor to Metallocenoporphyrin. Migration of the exo double bond was catalyzed by *p*-toluenesulfuric acid (Scheme 2).[41] Porphyrins **8**, **9**, **4**, and **10** were refluxed in CHCl$_3$ in the presence of *p*-TsOH for 1 day, and porphyrins **11**, **12**, **13**, and **14** were obtained in 80−95% yield, along with recovery of a small amount of starting material (less than 10%). Migration of the double bond in **8**, **9**, **4**, and **10** was confirmed by the splitting of the porphyrin β-protons, shifting

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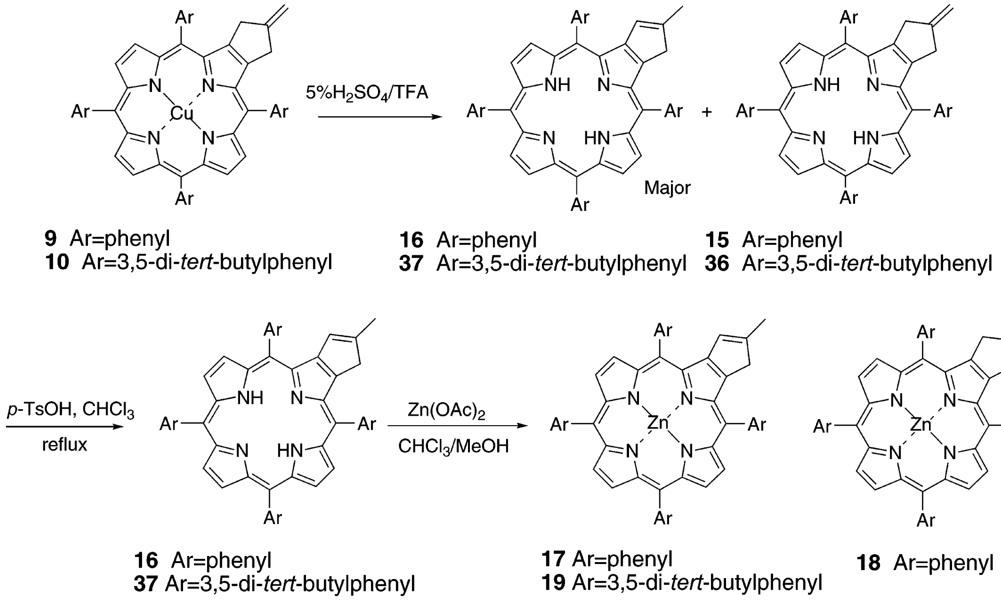
Scheme 3



of the two peaks at 3−5 ppm, and appearance of a new peak at ∼2.0 ppm (s, 3H) in their ^1H NMR spectra.

Fused Zn(II) Cyclopentadienylporphyrins. As mentioned above, Zn(II) 2-nitroporphyrins gave very poor yields of cycloaddition products. To prepare the Zn(II) analogues of **8** and **4**, the corresponding Cu(II) porphyrins were first demetalated, followed by reinsertion of Zn(II) (Scheme 3). Thus, Cu(II) porphyrin **9** was treated with 5% H_2SO_4 in TFA for 10 min at room temperature, and free base porphyrin was obtained quantitatively. The product turned out to be a mixture of the desired porphyrin **15** and its regioisomer **16** (major). Double-bond migration occurred in tandem with demetalation under the strongly acidic conditions. The free base character of the porphyrins was confirmed with the appearance of a broad peak at −2.91 ppm (NH) in the ^1H NMR spectra. These two isomers were not further separated. The mixture of **15** and **16** was then treated with *p*-TsOH to ensure complete conversion of **15** into its regioisomer **16**, followed by insertion of Zn(II) to give **17**. Porphyrin **19** was obtained in a similar way.

Fused Metallocenylporphyrins. Porphyrins **13**, **14**, and **19** were deprotonated with lithium diisopropylamide (LDA)[31,42,43] at 0 °C (Scheme 4). The participation of electrons from the porphyrin in the aromatic delocalization pathway of the fused cyclopentadienide ring induced a color change from red (porphyrin-like compound) to green (chlorin-like compound). The above mixture reacted with $Cp^*Ru^{III}Cl_2$ under argon at room temperature, leading to the desired ruthenocenoporphyrins **20**, **21**, and **22** in 25%, 14%, and 2% yields, respectively. Formation of **20**, **21**, and **22** was confirmed by MALDI-TOF mass spectrometry. The structure of **20** was confirmed by X-ray single-crystal diffraction.[26] In contrast to **20** and **21**, both of which survive chromatography and are stable in air, Zn(II) porphyrin **22** decomposed on silica gel. Pure **22** could not therefore be obtained. A porphyrin dimer **23** was isolated along with the ruthenoceno−Ni^{II}-porphyrin **20**. We speculate that this oxidative ($Cp^*Ru^{III}Cl_2$ serving as the oxidant) is similar to the dimerization of substituted cyclopentadienide derivatives using $FeCl_3$ as the oxidant.[44] Reactions carried out with deprotonated porphyrin **13** in the presence of $FeCl_3$ (replacing $Cp^*Ru^{III}Cl_2$) led to the same dimer **23** (Scheme 5).

A similar dimerization was not observed with Cu(II) and Zn(II) porphyrins **14** and **19**.

Porphyrins **11**, **12**, and **17** were deprotonated at 0 °C with LDA followed by addition of $FeCl_2$ at reflux to give the bisporphyrinatoferrocenes **24**, **25**, and **26**. Mass spectrometry (MALDI-TOF) confirmed their identity (*m*/*z* 1499.9, 1508.9, and 1512.2, respectively). In their ^1H NMR spectra, protons of the fused cyclopentadienyl ring were observed as a singlet at 3.01 ppm for **24** and at 3.28 ppm for **26**. Compounds **24** and **25** are only slightly soluble, whereas **26** is soluble in most organic solvents. This may be explained by noting the different π-stacking features of these compounds arising from the different coordination chemistry of their central metal ions. All three compounds displayed greater stability in the air compared with their respective Ru analogues.

Attempted Demetalation of Metallocenoporphyrins. The optical properties of porphyrin molecules can be tuned, apart from the peripheral substituents, by changing the metal center, its oxidation state, and axial ligands. Metallocenoporphyrins **24**, **25**, **26**, **20**, and **21** were subjected to demetalation under acidic conditions. Metalloceno-Ni(II)-porphyrins **24** and **20** underwent complete decomposition, whereas demetalation of **25**, **26**, and **21** led to degradation of the metallocene part of the molecules.

Bisruthenocenoporphyrin. Porphyrin **4** was nitrated with N_2O_4 in CH_2Cl_2 (Scheme 6), and a mixture of three

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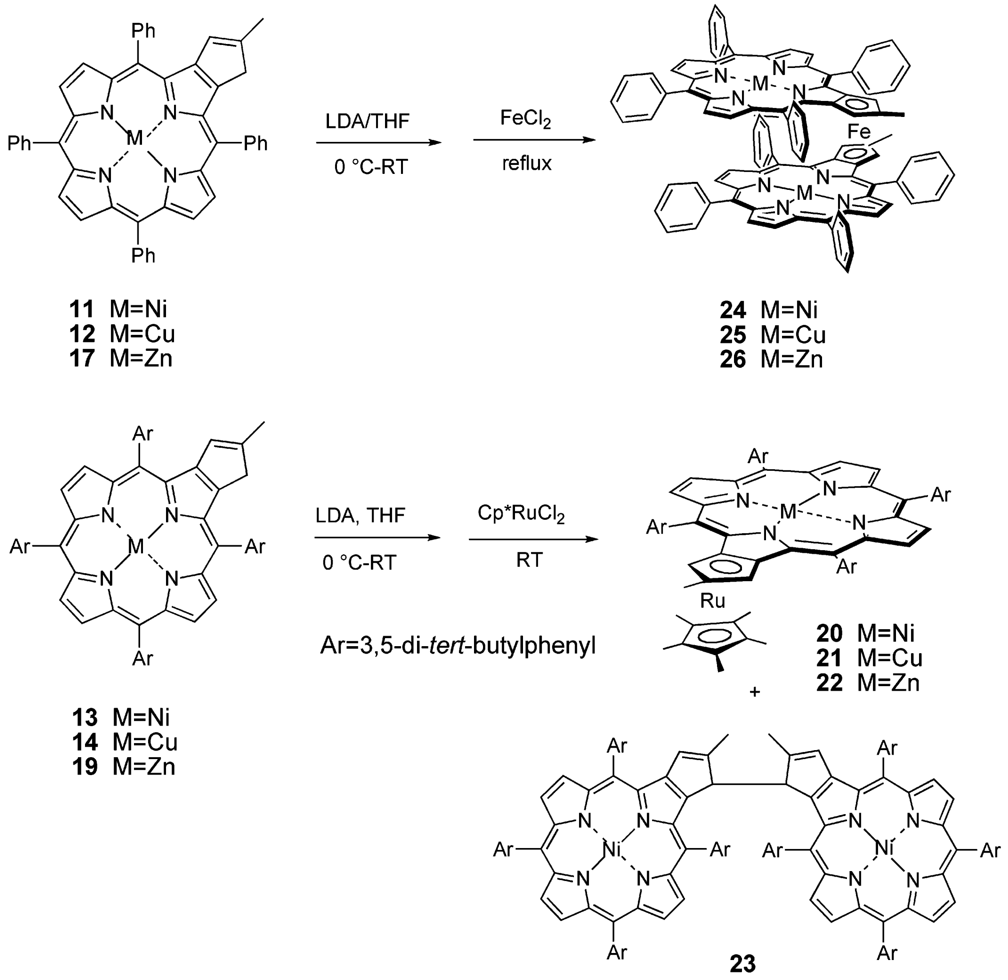
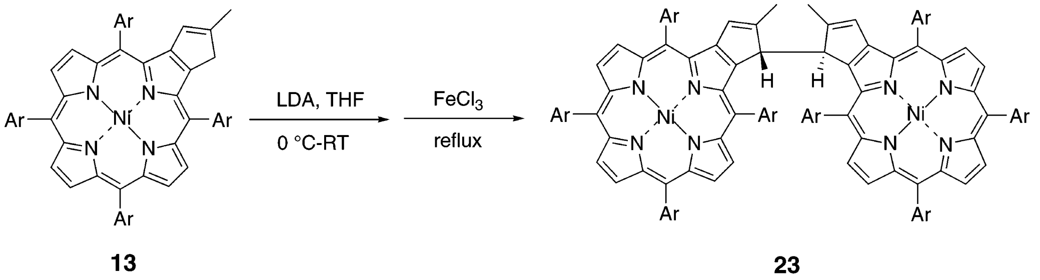
Scheme 4



Scheme 5

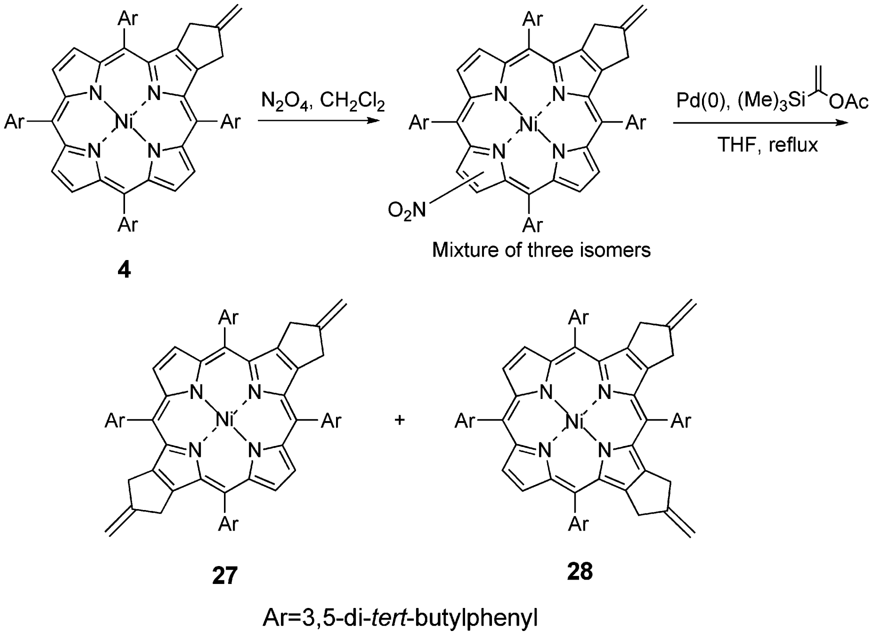


mononitration products was obtained, as expected. A [3 + 2] cycloaddition reaction carried out with this mixture gave two regioisomers **27** and **28**. Compounds **27** and **28** were separated on silica gel plates, eluting with cyclohexane/ CH_2Cl_2 (v/v, 10:1). Weak-acid-catalyzed double-bond migration converted **27** into two regioisomers **29** and **30** (Scheme 7). These two regioisomers, which were not further separated, were treated with LDA and $(C_5H_5)Ru^{III}Cl_2$ at room temperature. Two compounds, **31** and **32**, were expected from this reaction. Mass spectra of the reaction mixture implied the formation of bisruthenocenoporphyrin (MALDI-TOF, *m*/*z* 1693). However, though the desired bisruthenocenoporphyrin compound was formed, it was not stable enough to survive the workup conditions.

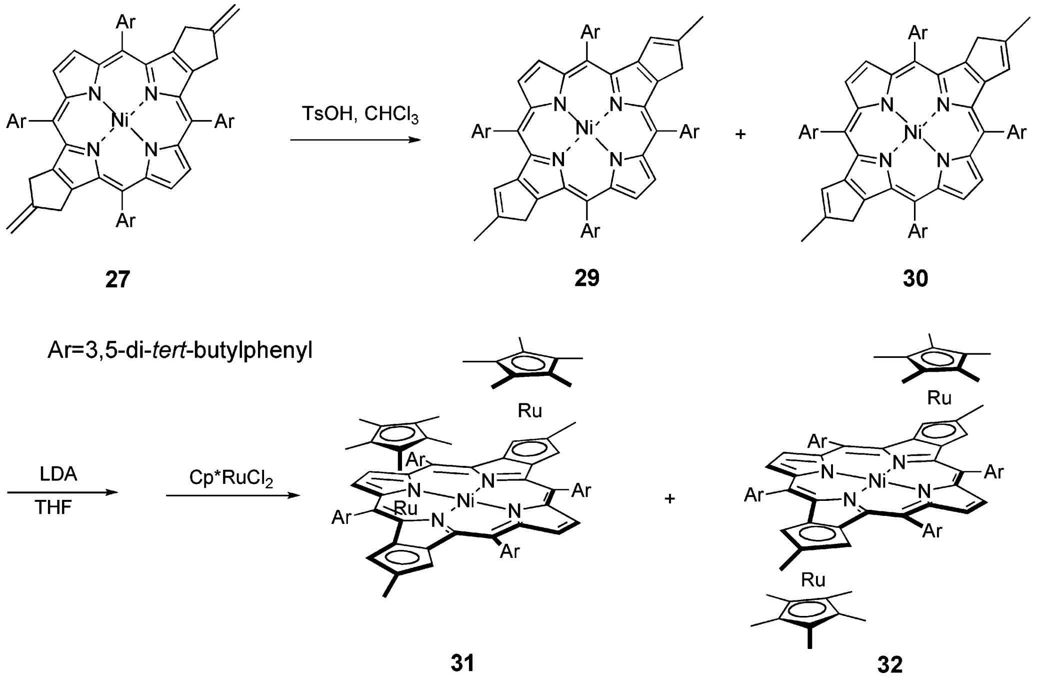
UV−vis Spectra. Compounds **21**−**22** and **24**−**26** possess interesting electronic absorption spectra (Supporting Information, Figure S1). Monoruthenocenoporphyrin **20** showed unusual absorptions; its Soret band has a broad shoulder spanning a range of 380−500 nm. All other metallocenoporphyrins displayed broad Soret bands and largely flattened Q bands. No significant bathochromic shift relative to their precursor porphyrins was observed for these metallocenoporphyrins. It should be noted that the extinction coefficients (ϵ) decrease significantly (by more than 50%) for each metallocenoporphyrin. These data suggest that intramolecular charge transfer might occur in these molecules.

X-ray Crystal Structure of Bisporphyrinatoferrocene 26. Figure 1 shows different views of the crystal structure of **26**. There are two different molecules (Figure 1) in each asymmetric unit. In both molecules the central Zn(II) ions are five-coordinated with the fifth ligands bound at the axial position outside of the ferrocene sandwich. In one molecule,

Scheme 6



Scheme 7



both the central zinc ions have THF as the fifth ligand with metal-to-plane (defined by the $C_{20}N_4$ porphyrin skeleton) displacements of 0.058 and 0.300 Å toward THF, respectively; in the other molecule, one central Zn(II) coordinates with MeOH, whereas the other one is coordinated with THF. The displacements of Zn out of the porphyrin plane are 0.065 Å toward MeOH and 0.137 Å toward THF. These two porphyrin macrocycles in each molecule are not strictly parallel. The dihedral angles between them are 10.2° and 3.3°, respectively. In each molecule, one porphyrin ring is rotated with respect to the other by about 72° in the 5-fold axis of the Cp ring. The ferrocene part of this molecule adopts an essentially eclipsed conformation by deviation of 6°. The two Cp rings in each molecule are off-parallel by 10.4° and 8.1° (with rough interplanar distances of 3.38 and 3.31 Å), respectively. The molecular arrangement in one asymmetric unit is displayed in the Supporting Information (Figure S2).

Electrochemistry

Monomeric Ni(II) Porphyrins 2, 13, and 20. Ni(II) porphyrins with numerous structures have been electrochemically characterized in our laboratories.[45−50] The reductions invariably involve the stepwise addition of one or two electrons to the porphyrin macrocycle, giving π-anion radicals and dianions. The oxidations often occur via a stepwise abstraction of two electrons from the conjugated macrocycle, giving a π-cation radical and dication, but in

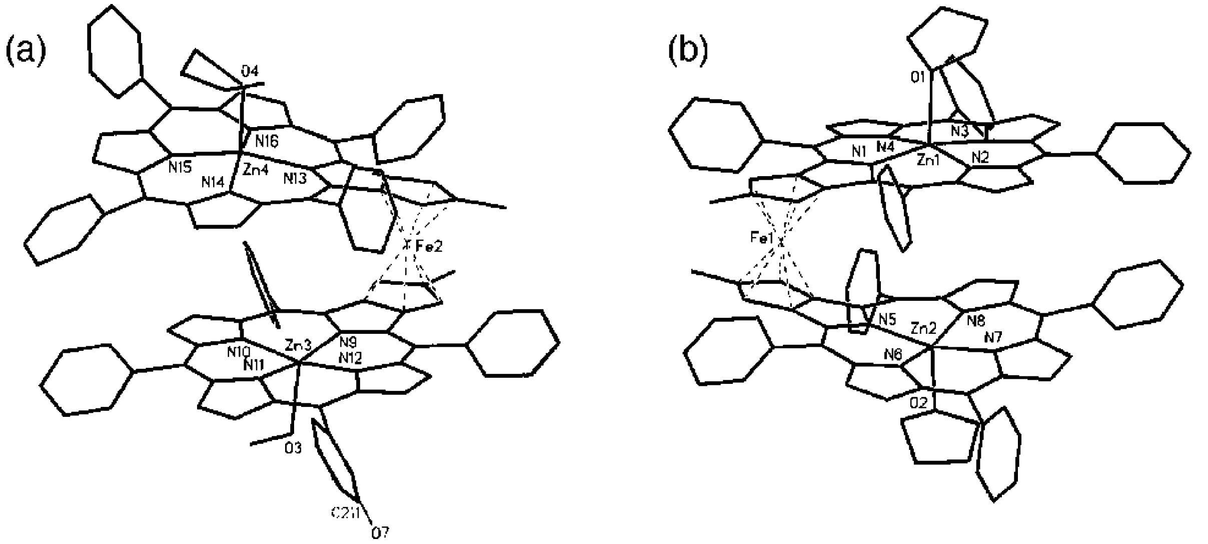


Figure 1. X-ray crystal structure of bisporphyrinatoferrocene **26**. (a) One molecule in the unit cell with THF and MeOH as the fifth axial ligands; (b) the other molecule in the unit cell with THF as both of the axial ligands.

many cases these processes are overlapped in potential leading to an overall two-electron conversion from a Ni(II) porphyrin to the Ni(II) porphyrin dication.[46] In either case the formation of a Ni(III) dication may be generated at more positive potentials although this reaction is not always observed.

Both the specific solvent-supporting electrolyte system and nature of axial ligation to the Ni(II) porphyrin play key roles in the prevailing oxidative behavior of the complexes, and specific changes in solvent and/or axial coordination can in some cases "direct" the initial electron abstraction to involve the metal center, here leading to an initial Ni(II)/Ni(III) reaction, followed at more positive potentials by the two ring-centered oxidations.[45]

Ni(II) porphyrin **13** with a fused cyclopentadienyl ring shows two well-resolved one-electron oxidations located at $E_{1/2} = 0.99$ and 1.19 V in PhCN containing 0.1 M TBAP. This contrasts with what is observed for *tert*-butyl Ni(II) porphyrin **2** where two overlapping one-electron oxidations are observed at the same $E_{1/2}$ value of 1.13 V (Figure 2). Compound **13** also undergoes two one-electron reductions, located at $E_{1/2} = -1.36$ and -1.95 V in PhCN (see Figure 2 and Supporting Information, Table S1). The first reduction and first oxidation of **13** are shifted negatively in potential by 50 and 140 mV, respectively, as compared to $E_{1/2}$ values for oxidation and reduction of the structurally related *tert*-butyl Ni(II) porphyrin **2** under the same solution conditions. The direction of the potential shift upon going from **2** to **13** can be accounted for by the electron-donating nature of the fused cyclpentadiene group on **13,** and this electron-donating effect influences to a greater extent the oxidation than the reduction, as indicated by the $\Delta E_{1/2}$ values between the two related compounds.

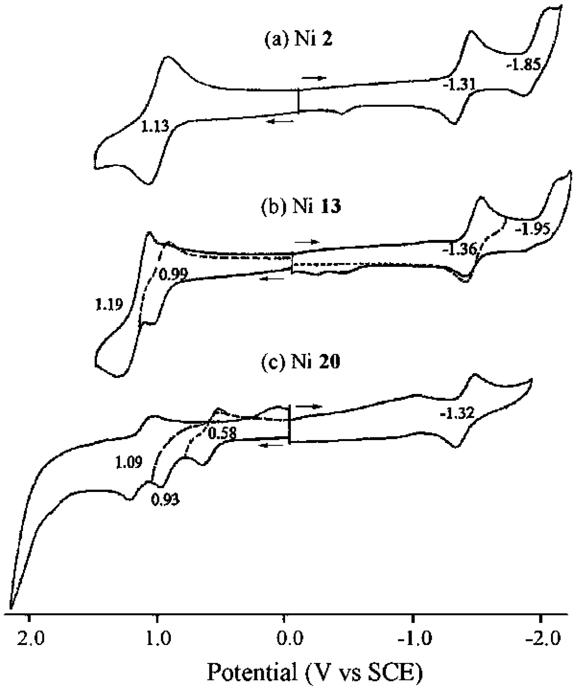


Figure 2. Cyclic voltammograms of Ni(II) porphyrins **2**, **13**, and **20** in PhCN containing 0.1 M TBAP. Scan rate = 0.10 V/s.

Differences are also obtained in the HOMO−LUMO gap of **2** and **13** under the same solution conditions. This value is 2.35 V for **13** and 2.44 V for **2**. Both HOMO−LUMO gaps fall within the range reported for most Ni(II) porphyrins where the oxidations and reductions all occur at the conjugated macrocycle.[45,46]

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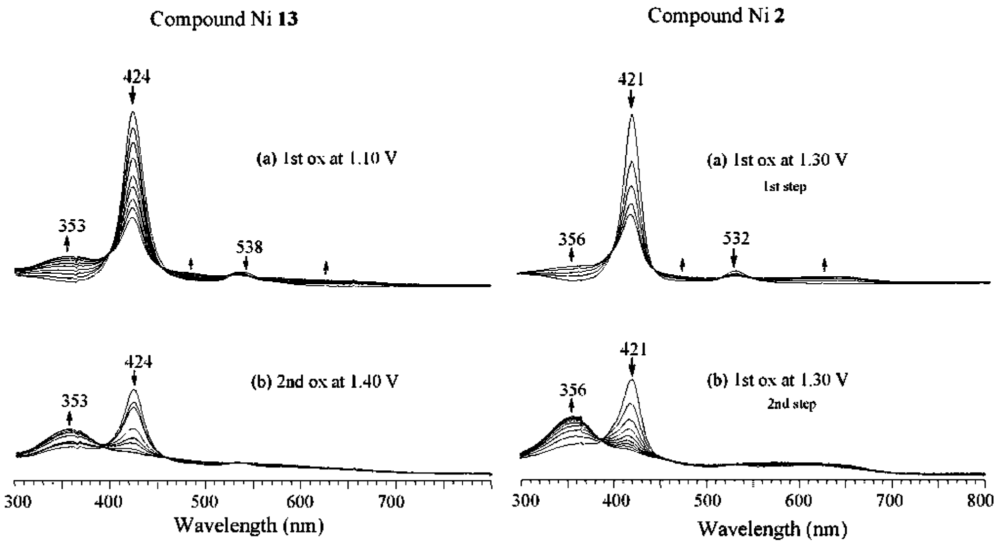

Figure 3. Thin-layer UV−vis spectral changes obtained during the electron transfer reactions of Ni **13** and Ni **2** in PhCN, 0.1 M TBAP. The direction of spectral changes is illustrated by the arrows.

Compound **20** differs from **2** and **13** in that it contains a fused electroactive ruthenocene unit which not only increases the number of observed oxidations but also leads to shifts in potentials for oxidation of both the porphyrin and the ruthenocene parts of the molecule as compared with the two electroactive units themselves when they are not fused to each other, i.e., ruthenocene and *tert*-butylphenylporphyrin **2**. In contrast with the oxidations, the presence of the linked ruthenocene group on **20** has little or no effect on the reduction potentials as seen in Figure 2 where **20** undergoes an initial one-electron addition at −1.32 V as compared to $E_{1/2} = -1.31$ V for **2** and −1.36 V for **13**. The expected second reduction of **20** was not observed but should be close to the negative potential limit of the PhCN solvent.

The most significant difference between **2**, **13**, and **20** is in the oxidation behavior of the compounds. Three well-defined one-electron oxidations are observed for **20,** the first and third of which are reversible in PhCN, 0.1 M TBAP (Figure 2). Ruthenocene is reported to undergo an irreversible two-electron oxidation between 0.60 and 0.78 V in CH_3CN,[51−53] and two oxidations at similar potentials are also seen in the case of **20**. The fused ruthenocene group is therefore proposed as the initial site of electron abstraction in **20,** where the two one-electron oxidations associated with this ruthenocene-centered reaction are located at $E_{1/2} = 0.58$ and $E_{pa} = 0.93$ V vs SCE in PhCN for a scan rate of 0.1 V/s. The fact that the initial ruthenocene-centered one-electron oxidation is reversible in the case of **20** and not in the case of ruthenocene itself indicates that the porphyrin macrocycle acts as a stabilizing ligand for the single oxidized (ruthenocene)$^+$ and also prevents dimerization which occurs in the absence of the porphyrin.[54]

The UV−vis spectral changes obtained during oxidation or reduction of nickel porphyrins have often been used to determine the site of electron transfer.[45] When the intensity of the porphyrin Soret band significantly decreases after a reduction or oxidation, the electron-transfer site is generally porphyrin-ring-centered, leading to formation of a π-anion or π-cation radical.[45] However, when the Soret band is only slightly shifted in wavelength and undergoes little or no change in absorptivity upon reduction or oxidation, the electron-transfer reactions can then often be assigned as metal-centered, leading either to the formation of singly charged Ni(I) or Ni(III) porphyrins or, alternately, to redox reactions involving another electroactive site on the molecule in addition to the conjugated porphyrin macrocycle.

During the first oxidation of Ni **13** at 1.10 V, the bands at 424 and 538 nm both decrease in intensity while a new broad band grows in at 353 nm. A further decrease in intensity of the 424 nm Soret band intensity is seen during the second oxidation at −1.40 V. The spectral changes are identical with those observed upon oxidation of Ni **2** (Figure 3) and indicate, in both compounds, the stepwise formation of a π-cation radical and dication upon the first and second one-electron oxidations.

The first reduction of compound **13** at a controlled potential of −1.50 V also leads to a significant loss of Soret band intensity as seen in Figure 4. After completion of electrolysis, the initial Soret band at 424 nm has shifted to 410 nm, the initial visible band at 538 nm has disappeared, and two new broad visible bands are seen at 490 and 585 nm. The UV−vis spectral changes of **13** during this reduction are similar to what is seen during reduction of compound **2** (Figure 4b) and indicate electron addition to the macrocycle in both cases, i.e., formation of a Ni(II) π-anion radical after addition of one-electron to the initial compound.

The spectral changes of compound **20** obtained after electrooxidation differ from those of **2** and **13**. The neutral compound **20** has a split Soret band at 418 and 456 nm (Figure 5a) whereas the neutral compounds **13** and **2** have

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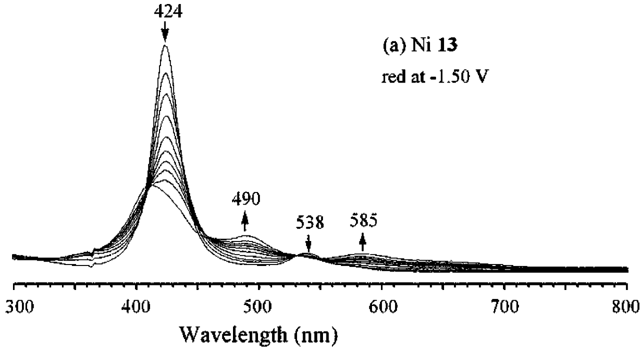

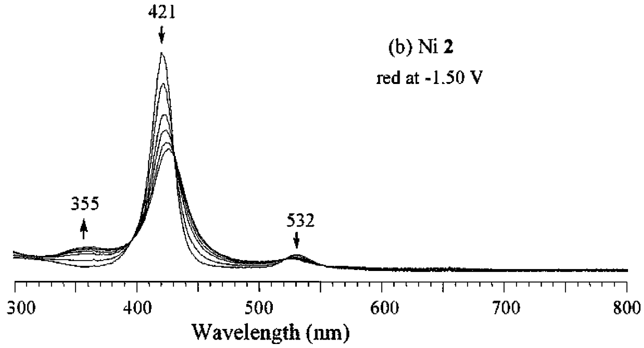

Figure 4. Thin-layer UV−vis spectral changes of Ni **13** and Ni **2** obtained upon reduction in PhCN, 0.1 M TBAP.

an unsplit Soret band located at 424 and 421 nm, respectively (Figures 3 and 4). After the first oxidation of **20** at 0.80 V, the absorption at 418 shifts to 426 nm whereas after further oxidation at 1.02 V the Soret band maximum shifts to 429 nm as seen in parts a−c of Figure 5. In neither case is there a significant loss of Soret band intensity, and the shift in position of the Soret band can be accounted for by an increased positive charge on the porphyrin after each oxidation. Both results strongly suggest that the first two oxidations of **20** are ruthenocene-centered. This is also the conclusion which results from the fact that the first two oxidations of **20** are similar to potentials for the oxidation of ruthenecene itself in the absence of the porphyrin.[51−53] The third oxidation of compound **20** (Figure 2) must therefore be a porphyrin ring-centered electron transfer, and this is the conclusion that results from analyzing the spectral changes in Figure 5d during oxidation of the compound at 1.38 V in PhCN.

Linked Ni(II) 24 and Cu(II) 25 Dyads. Compound **24** contains two identical Ni(II) tetraphenylporphyrins connected by a fused ferrocene group. Two reversible oxidations are observed for this compound. The first is located at $E_{1/2} = 0.39$ V vs SCE and assigned to the Fc/Fc^+ reaction of the linking group. The second oxidation occurs at $E_{1/2} = 1.22$ V and is, on the basis of its similarly to the (TPP)Ni oxidation (Figure 6a), assigned as a π-ring-centered reaction of the porphyrin.

Compared to the first oxidation potential of ferrocene itself under the same solution conditions ($E_{1/2} = 0.49$ V), the oxidation of the ferrocene unit in compound **24** is negatively shifted by 100 mV to $E_{1/2} = 0.39$ V. This result indicates that the two porphyrin rings act as electron-donating substituents, thus producing an easier oxidation of the linked ferrocene group on **24**. The second quasi-reversible oxidation of Ni **24** at 1.22 V is an overall four-electron process. One electron is initially abstracted from the linked Fc unit, and four electrons are then abstracted at the same or very similar potentials from the two porphyrin π-ring systems, thus giving as final product two Ni(II) porphyrin dications linked by a singly oxidized ferrocene group. This process is well-precedented in similar dimeric systems.[55] The overall porphyrin-centered oxidation of **24** is 100 mV greater than the porphyrin-centered oxidation of (TPP)Ni. This is consistent with the electron-withdrawing effect of the ferrocene group in **24**, thus leading to a harder porphyrin-centered oxidation and an easier Fc-centered oxidation in the molecule.

Each porphyrin macrocycle of **24** undergoes a reversible one-electron reduction, but the potentials are not overlapped in this case. One porphyrin unit is reduced at $E_{1/2} = -1.24$ V and the other at $E_{1/2} = -1.35$ V (see Figure 6a). This

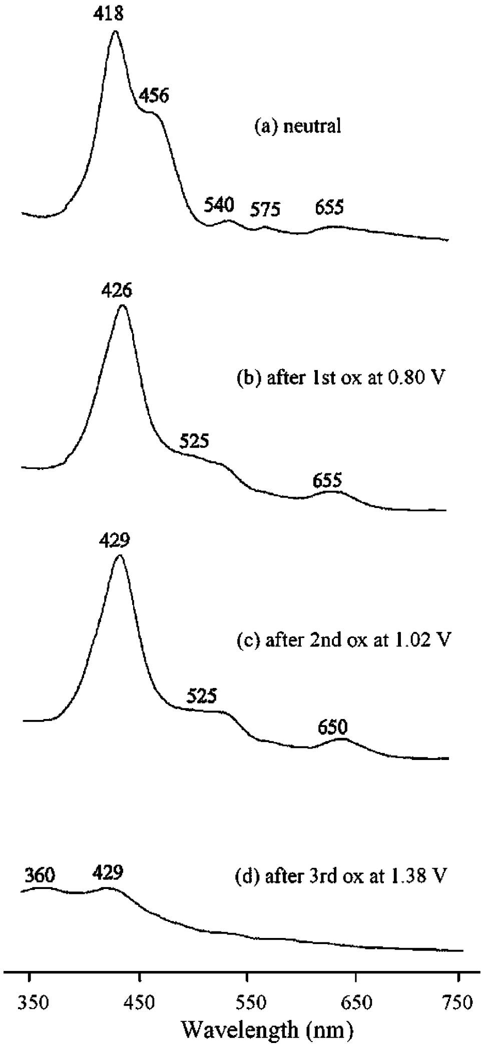

Figure 5. UV−vis spectra of neutral and electrooxidized Ni **20** in PhCN, 0.1 M TBAP.

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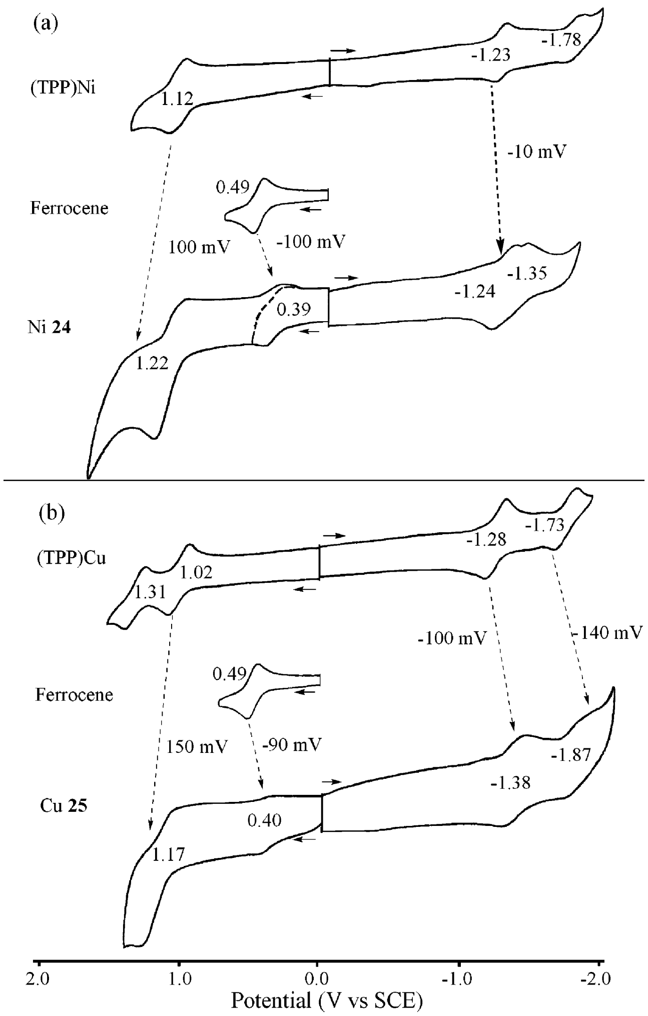


Figure 6. Cyclic voltammograms for oxidation and reduction of Ni **24**, Cu **25**, and corresponding (TPP)M and Fc units in PhCN, 0.1 M TBAP, at a scan rate of 0.10 V/s.

difference in $E_{1/2}$ indicates a strong interaction between the π-ring systems of the two equivalent porphyrin macrocycles.

Similar electrochemical behavior is seen for the copper dyad **25** (Figure 6b). The initial reversible one-electron oxidation at $E_{1/2} = 0.40$ V is ferrocene-centered, whereas the following four-electron oxidation at $E_{1/2} = 1.17$ V is porphyrin-centered. Two reductions are observed at $E_{1/2} = -1.38$ and -1.87 V, and these are proposed to involve two electrons in each process, thus leading to first a bisporphyrin π-anion radical and then, at more negative potentials, to a bisporphyrin dianion. The fact that each porphyrin macrocycle of **25** is reduced at the same potential is consistent with only a weak interaction between the two equivalent π-ring systems that are connected to each other via the ferrocene group.

Time-resolved UV−vis spectra upon controlled potential oxidation and reduction of Cu **25** were recorded in PhCN, 0.1 M TBAP, and are consistent with the cyclic voltammetric data. These spectral changes are shown in Figures 7 and 8. The initial broad Soret band of Cu **25** at 417 nm decreases only slightly in intensity upon the first oxidation at 0.70 V (Figure 7a) as would be expected for an oxidation at the ferrocene part of the molecule.

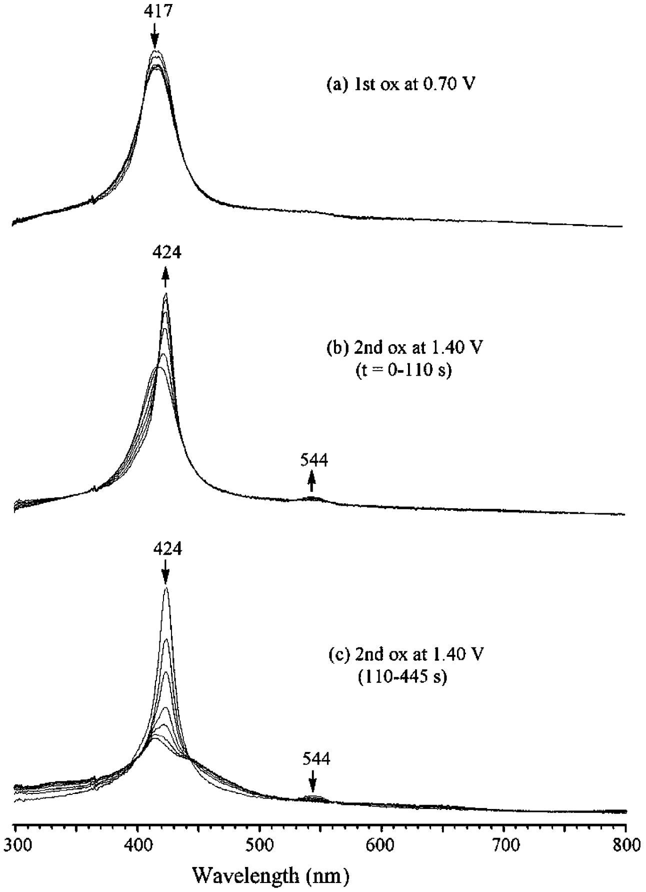


Figure 7. Thin-layer UV−vis spectral changes of Cu **25** obtained upon oxidations in PhCN, 0.1 M TBAP.

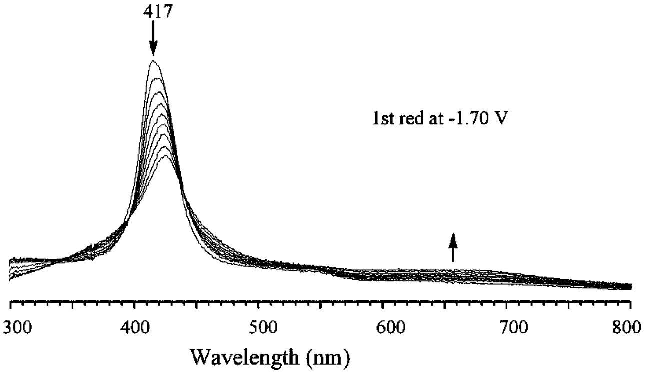
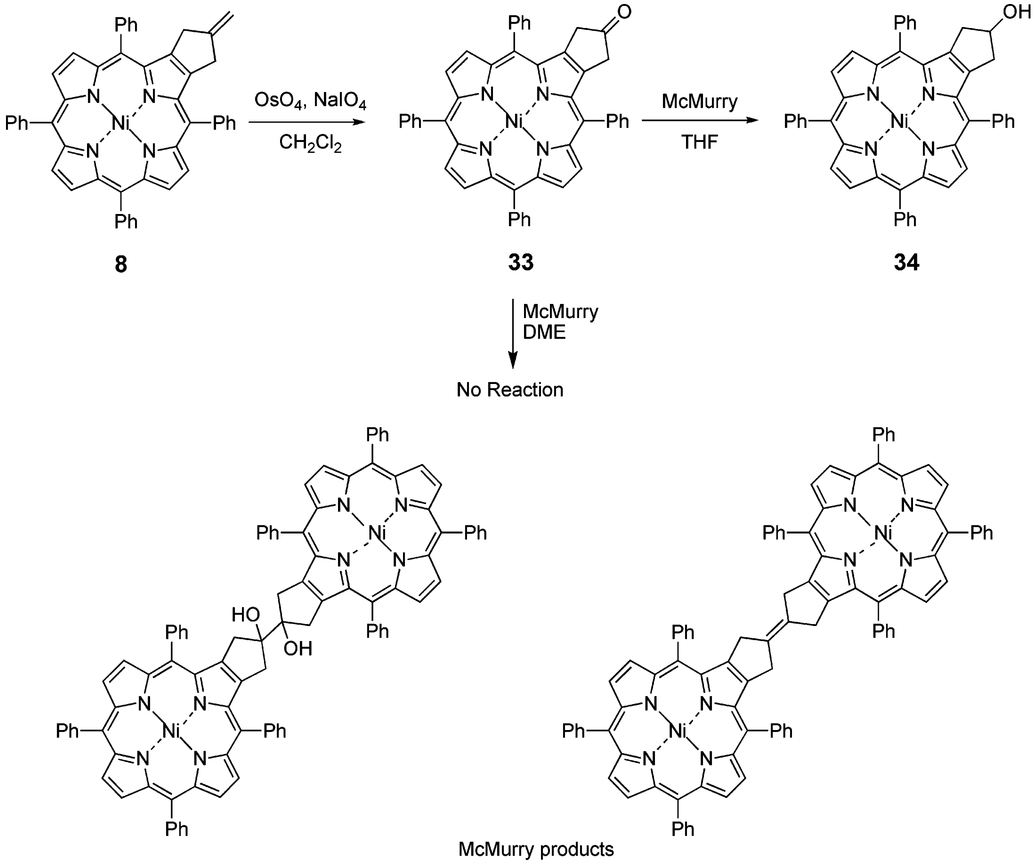


Figure 8. Thin-layer UV−vis spectral changes of Cu **25** obtained upon reduction in PhCN, 0.1 M TBAP.

Two different sets of spectral changes are observed upon the second oxidation at 1.40 V, each of which displays isosbestic behavior. The first occurs from 0 to 110 s and leads to a “normal” copper tetraphenylporphyrin spectrum with a strong Soret band at 424 nm and a well-defined visible band at 544 nm (Figure 7b). The second set of spectral changes occurs from 110 to 445 s and results in much decreased intensity of the Soret band (Figure 7c). The latter reaction is clearly porphyrin ring-centered under the given experimental conditions. The “sharpening” of the Soret band upon going from Cu **25** to Cu **25**$^{+}$ is also consistent with an oxidation at the linking Fc group and a concomitant decrease in interaction between the two porphyrin π-ring systems.

Scheme 8



Derivatives of *β,β′*-Fused Propanoporphyrins. As illustrated in Scheme 8, porphyrin **8** was oxidized to keto-porphyrin **33** using OsO_4 (catalytic amount)/$NaIO_4$. This reaction proceeded smoothly. Porphyrin **33** was then subjected to the McMurry reaction in DME[56−59] in the hope that a dimeric McMurry product with an extended π-system would be obtained. However, only starting material was recovered. This might result from the low solubility of porphyrin **33** in DME. McMurry reactions carried out in THF also failed to give the desired McMurry product; they instead led to the hydroxy-porphyrin **34** in reasonable yield. Addition of a base to the reaction mixture generated the same product. However, it should be mentioned that, by examination of the structure of **33**, the enol form of this keto-porphyrin is relatively stable due to the conjugation of the enol double bond into the porphyrin macrocycle. This may account partially for the failure of the McMurry reaction and explain the fact that porphyrin **34** was reproducibly obtained in these reactions.

Conclusions

In this work, a Pd(0)-catalyzed [3 + 2] cycloaddition reaction was successfully applied to 2-nitro-*meso*-tetraarylporphyrins to fuse a five-membered carbocycle onto the porphyrin periphery. A series of β,β'-fused monoruthenoceno−metalloporphyrins and bismetalloporphyrinatoferrocenes with different central metals were prepared. Whereas all three bismetalloporphyrinatoferrocenes (**24**, **25**, and **26**) and monoruthenoceno−metalloporphyrins (**20** and **21**) are stable for a certain amount of time in the air, monoruthenoceno−Zn(II)-porphyrin **22** decomposed readily, possibly due to the electron-rich nature of both the central metal (Zn(II)) and the porphyrin ring. Efforts to synthesize metallocene free base porphyrin compounds failed. The formation of bismetalloceno−Ni(II)-porphyrins (**31**, **32**) was detected by MS (MALDI-TOF). A porphyrin dimer (**23**) was identified along with monoruthenoceno−Ni(II)-porphyrin **20**. All three bismetalloporphyrinatoferrocenes (**24**, **25**, and **26**) exhibited similar UV−vis spectra with broad Soret bands and no well-defined Q bands. The electrochemistry of **20** was compared with its precursor compounds **2** and **13** and showed significant difference. The fact that the initial ruthenocene-centered one-electron oxidation is reversible in the case of **20** and not in the case of Rc itself indicates that the porphyrin macrocycle acts as a stabilizing ligand for the single oxidized Rc^+ and also prevents dimerization, which occurs in the absence of the porphyrin. Whereas porphyrinatoferrocene **25** only displayed weak interaction between the two equivalent porphyrin π-ring systems, strong interaction was detected for porphyrinatoferrocene **24,** another example of the important role the central metallic ion can play in electronic

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properties of porphyrin molecules. A crystal structure of bis-Zn(II)-*meso*-tetraphenylporphyrinatoferrocene (**26**) was obtained. The porphyrin macrocycles in the two molecules within the crystal are essentially planar due to the coordination to the organometallic moieties. In these molecules, one porphyrin ring is rotated with respect to the other by about 72° in the 5-fold axis of the Cp ring.

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Supporting Information Available: UV−vis spectra of compounds **20**, **21**, and **24**−**26**; X-ray crystal structure of compound **26** showing one asymmetric unit; table of electrochemical half-wave potentials; CIF for compound **26**. This material is available free of charge via the Internet at http://pubs.acs.org.

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