Peripheral Palladium(II) and Platinum(II) Complexes of Bis(dimethylamino)porphyrazine

Steven J. Lange,[†] Hanlin Nie,[†] Charlotte L. Stern,[†] Anthony G. M. Barrett,*[,‡] and Brian M. Hoffman*[,†]

Departments of Chemistry, Northwestern University, Evanston, Illinois 60208, and Imperial College of Science, Technology and Medicine, South Kensington, London SW7 2AY, U.K.

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The unsymmetrical porphyrazine (tetraazaporphyrin) bearing a single peripheral bis(dimethylamino) functionality, $Mg[pz(NMe_2)_2(Pr)_6]$, was prepared by base-catalyzed cross condensation of dipropyl maleonitrile (in excess) with dimethylamino maleonitrile. The freebase ($2H[pz(NMe_2)_2(Pr)_6]$) and centrally metalated forms ($M[pz(NMe_2)_2(Pr)_6]$; M = Ni(II), Cu(II), Mn(III)) were prepared by treatment of $Mg[pz(NMe_2)_2(Pr)_6]$ with trifluoroacetic acid and then the appropriate metal salt. $PdCl_2$ and $PtCl_2$ were coordinated to the peripheral bis(dimethylamino) chelates, yielding the bimetallic complexes, $M[pz(NMe_2)_2(Pr)_6]M'Cl_2$ (M = Ni, Cu; M′ = Pd, Pt). The heteroleptic $[N_2-Pd-S_2]$-capped porphyrazines were prepared readily by substituting the chloride ions of $M[pz(NMe_2)_2(Pr)_6]PdCl_2$ with the dithiolene chelates, maleonitriledithiolate (mnt^{2-}), benzenedithiolate (bdt^{2-}), and 1,3-dithiole-2-one-4,5-dithiolate ($dmid^{2-}$). The $[N_2-Pt-S_2]$ complexes were prepared by reaction of $M[pz(NMe_2)_2(Pr)_6]PtCl_2$ with the dialkyltin-protected dithiolates dibutyltin(toluene-3,4-dithiolate) and dibutyltin(dmit). The peripheral heteroleptic $[N_2-M'-S_2]$ core was found to be electroactive for electron-rich dithiolene ligands (bdt^{2-}, $E_{1/2}(Pd^{III}/Pd^{II}) = 0.22$ V; tdt^{2-}, $E_{1/2}(Pt^{III}/Pt^{II}) = 0.20$ V; $dmid^{2-}$, $E_{1/2}(Pd^{III}/Pd^{II}) = 0.19$ V; $dmit^{2-}$, $E_{1/2}(Pt^{III}/Pt^{II}) = 0.19$ V) but not for the relatively electron-poor dithiolene, maleonitriledithiolate (mnt^{2-}). The X-ray structure of $Ni[pz(NMe_2)_2(Pr)_6]$-Pd(mnt) (**13**) was determined. Crystal data for $C_{85}H_{109}Cl_3N_{24}Ni_2Pd_2S_4$: space group $P2_1/n$; $a = 17.435(4)$ Å, $b = 17.982(2)$ Å, $c = 30.577(2)$ Å; $\beta = 104.27(2)°$; $Z = 4$.

Introduction

There is considerable interest in the design of ligand systems capable of binding multiple metal ions as their utility spans a wide range of applications including studies of electron transfer,[1] magnetic interactions,[2] and in biomimetic chemistry.[3,4] Our efforts in these areas utilize the tetraazaporphyrin (porphyrazine) macrocycle as a structural template for rigid organization of the metal centers, with potential to mediate electron transfer or magnetic exchange between metal ions. Peripherally functionalized porphyrazines are prepared by the template cyclization of maleonitrile derivatives and have the form $M[pz(\mathbf{A}_n;\mathbf{B}_{4-n})]$, where **A** and **B** symbolize functional groups fused directly to the β-positions of the pyrroles, and M represents a metal ion coordinated in the macrocyclic core. The peripheral **A** moieties generally involve heteroatoms (S, N, O) appended to the porphyrazine ring and can be designed to bind an exocyclic metal ion. The **B** groups can be designed to (i) optimize the yields; (ii) introduce novel electronic, optical, or redox properties; or (iii) to confer a desired solubility. We have previously reported the preparation of the octakis(dimethylamino)porphyrazine.[5,6] Here we report the preparation and properties of unsymmetrical porphyrazines having a single peripheral bis(dimethylamino) functionality, $M[pz(NMe_2)_2;(n\text{-}pr)_6]$, M = 2H, Mg(II), Ni(II), Cu(II), Mn(III). The peripheral $(NMe_2)_2$ moiety in these porphyrazines is analogous to the metal-binding chelates tetramethylethylenediamine (tmen) and tetramethyl-*o*-phenylenediamine (tmopda) and we further report the preparation of a series of peripherally $(NMe_2)_2MS_2$ (M = Pd, Pt) metalated porphyrazines, including a Pd(II)-linked porphyrazine dimer (Figure 1).

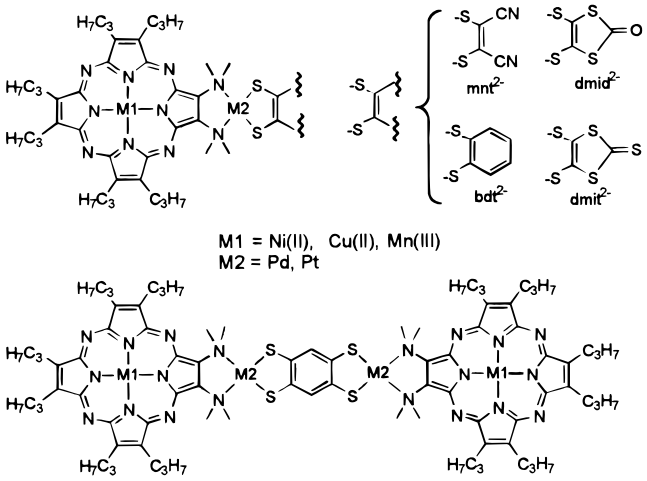

Figure 1. Peripherally N-functionalized porphyrazines.

[†] Northwestern University.
[‡] Imperial College of Science, Technology, and Medicine.

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Scheme 1

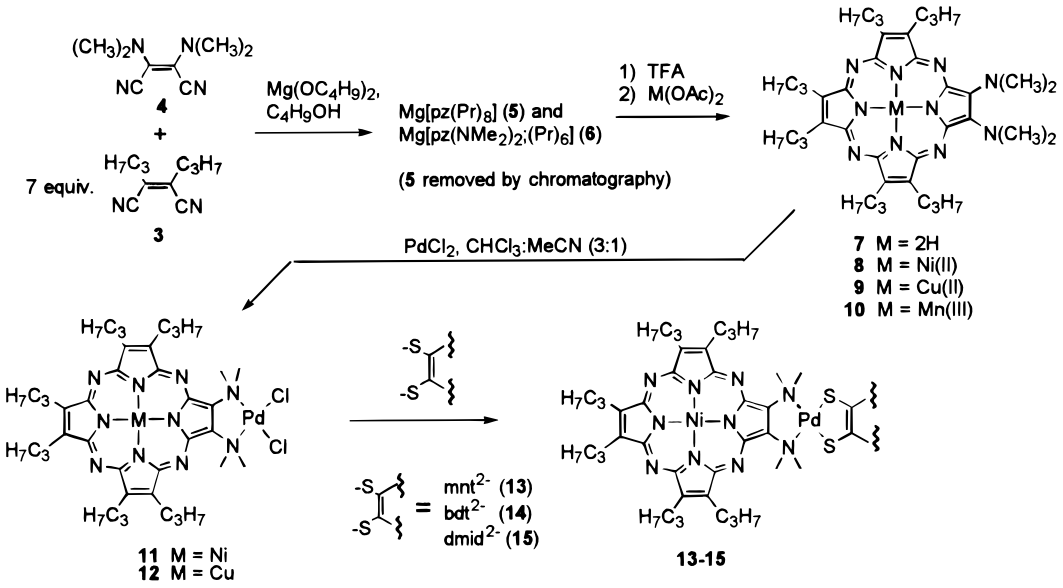

Table 1. Crystallographic Data for Compound **13**

formula	$C_{85}H_{109}Cl_3N_{24}Ni_2Pd_2S_4$	d_{calcd}/g cm^{-3}	1.45
mol wt	2031.78	λ/Å	0.71073 (Mo)
space group	$P2_1/n$ (No. 14)	μ/cm^{-1}	10.14
a/Å	17.435(4)	2θ max	45.9°
b/Å	17.982(2)	trans. coeff.	0.59−1.00
c/Å	30.577(2)	no. of unique data	13491
α/deg		no. of data with $I > 3.00\sigma(I)$	6656
β/deg	104.27(2)	no. of variables	1079
γ/deg		GOF	2.22
V/Å^3	9290.7(1)	R^a	0.056
Z	4	$R_w{}^b$	0.053
T/°C	−120		

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.

Experimental Section

Materials and Apparatus. Bis(dimethylamino)maleonitrile[7] (tmdamn) and dibutyltin(dmit) (H_2dmit = 4,5-dimercapto-1,3-dithiole-2-thione)[8,9] were prepared according to published procedures. All other reagents and solvents were obtained from commercial suppliers and used without further purification. Proton and carbon NMR spectra were recorded on a Varian Gemini-300 (300 MHz) spectrometer. Infrared spectra were recorded on a Mattson Instruments Alpha Centauri FTIR spectrometer. UV−visible spectra were recorded on a HP 8453A spectrophotometer. EI and FAB mass spectra were recorded using a VG-70-250SE instrument. Elemental analyses were performed by Oneida Research Services. Cyclic voltammetric measurements were carried out using a Cypress Systems 1087 computer-controlled potentiostat. A single compartment cell was used with a platinum disk working electrode, a Ag/AgCl reference electrode, and a silver wire as auxiliary electrode. Measurements were made in dichloromethane with tetra-*n*-butylammonium hexafluorophosphate as supporting electrolyte. Solutions containing approximately 10^{-3} M analyte (0.1 M electrolyte) were deaerated for several minutes by dinitrogen purge. All $E_{1/2}$ values were calculated from $(E_{pa} + E_{pc})/2$ at a scan rate of 110 mV s^{-1} and no correction for junction potentials. Ferrocene was added as an internal reference for all measurements.

X-ray Crystallography. A crystal suitable for X-ray analysis of compound **13** (Scheme 1) was grown by diffusion of methanol into a solution of **13** in chloroform in an 8 mm diameter glass tube sealed at one end. Crystallographic data are summarized in Table 1. The crystal was mounted on a glass fiber using oil (Paraton-N, Exxon). The data were collected using the $\omega-\theta$ scan technique by means of an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo Kα radiation. Orientation and intensity standards were measured every 90 min. No decomposition was observed during data collection. The data were corrected for Lorentz and polarization effects and an analytical absorption correction was applied. In compound **13** there is disorder in one propyl chain of each of the crystallographically independent molecules. In one molecule, one alternate site occupancy of 35% was identified for C(34); in the other, two alternate positions for C(63) and C(64) each of 50% occupancies were identified.

The structure was solved by direct methods (SHELXS 86) and refined by the full-matrix least-squares technique (TEXSAN 5.0). All non-hydrogen atoms other than C(34), C(63), and C(64) were refined anisotropically. Hydrogen atoms were included in idealized positions. All calculations were performed using the TEXSAN crystallographic software package of Molecular Structures Corporation. The final cycle of full-matrix least-squares refinement for **13** was based on 6656 unique data with $I > 3\sigma(I)$ and 1079 variables and converged with $R = 0.056$ and $R_w = 0.053$. Selected bond distances, angles and positional parameters area collected in Tables 2−4, respectively.

4,5-Dibromo-4*E*-octene (1). A solution of bromine (46.6 mL, 0.91 mol) in acetic acid (250 mL) was added dropwise to 4-octyne dissolved in an equal amount of AcOH (250 mL) at such a rate as not to develop an orange color in the flask. After the addition was complete the solution was stirred an additional 30 min and then poured into ice water (2 L). A yellow oil separated under the aqueous layer and was collected. The oil was taken up in CH_2Cl_2 (750 mL), and the resulting solution was washed with saturated aqueous $NaHCO_3$ (3 times, 250

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Table 2. Selected Intramolecular Bond Distances (Å) for Compound **13**

Pd(1)−S(1)	2.254(4)	Ni(1)−N(1)	1.894(9)
Pd(1)−S(2)	2.257(4)	Ni(1)−N(3)	1.84(1)
Pd(1)−N(9)	2.14(1)	Ni(1)−N(5)	1.900(9)
Pd(1)−N(10)	2.15(1)	Ni(1)−N(7)	1.86(1)
Pd(2)−S(3)	2.240(4)	Ni(2)−N(13)	1.902(9)
Pd(2)−S(4)	2.234(4)	Ni(2)−N(15)	1.87(1)
Pd(2)−N(21)	2.13(1)	Ni(2)−N(17)	1.889(9)
Pd(2)−N(22)	2.13(1)	Ni(2)−N(19)	1.85(1)

Table 3. Selected Intramolecular Bond Angles (deg) for **13**

S(1)−Pd(1)−S(2)	89.7(1)	Pd(1)−S(1)−C(40)	101.9(5)
S(1)−Pd(1)−N(9)	91.6(3)	Pd(1)−S(2)−C(39)	103.0(5)
S(1)−Pd(1)−N(10)	174.6(3)	Pd(1)−N(10)−C(38)	111.4(7)
S(2)−Pd(1)−N(9)	177.9(3)	Pd(1)−N(9)−C(35)	108.5(7)
S(2)−Pd(1)−N(10)	93.4(3)	Pd(1)−N(9)−C(36)	112.8(7)
N(9)−Pd(1)−N(10)	85.4(4)	Pd(1)−N(10)−C(3)	103.2(7)
S(3)−Pd(2)−S(4)	90.1(1)	Pd(1)−N(10)−C(37)	110.7(7)
S(3)−Pd(2)−N(21)	91.3(3)	Pd(2)−S(3)−C(81)	103.2(5)
S(3)−Pd(2)−N(22)	177.2(3)	Pd(2)−S(4)−C(82)	102.8(5)
S(4)−Pd(2)−N(21)	178.6(3)	Pd(2)−N(21)−C(44)	101.7(8)
S(4)−Pd(2)−N(22)	91.6(3)	Pd(2)−N(21)−C(77)	110.8(7)
N(21)−Pd(2)−N(22)	87.0(4)	Pd(2)−N(21)−C(78)	111.0(7)
N(1)−Ni(1)−N(3)	91.5(4)	Pd(2)−N(22)−C(45)	101.0(8)
N(1)−Ni(1)−N(5)	178.9(4)	Pd(2)−N(22)−C(79)	109.9(7)
N(1)−Ni(1)−N(7)	89.6(5)	Pd(2)−N(22)−C(80)	113.2(8)
N(3)−Ni(1)−N(5)	88.7(4)	Ni(1)−N(3)−C(8)	132.6(9)
N(3)−Ni(1)−N(7)	178.3(4)	Ni(1)−N(5)−C(9)	125.7(9)
N(5)−Ni(1)−N(7)	90.3(5)	Ni(1)−N(5)−C(12)	125.7(9)
N(13)−Ni(2)−N(17)	177.9(4)	Ni(1)−N(7)−C(13)	128.0(9)
N(13)−Ni(2)−N(15)	91.1(5)	Ni(1)−N(7)−C(16)	130.8(9)
N(13)−Ni(2)−N(19)	89.8(5)	Ni(2)−N(13)−C(43)	125.4(9)
N(15)−Ni(2)−N(17)	89.5(5)	Ni(2)−N(15)−C(47)	126.9(9)
N(15)−Ni(2)−N(19)	177.7(4)	Ni(2)−N(15)−C(50)	132.1(9)
N(17)−Ni(2)−N(19)	89.7(5)	Ni(2)−N(17)−C(51)	123.8(9)
Ni(1)−N(1)−C(1)	126.1(9)	Ni(2)−N(17)−C(54)	127.9(9)
Ni(1)−N(1)−C(4)	126.7(9)	Ni(2)−N(19)−C(55)	126.0(9)
Ni(1)−N(3)−C(5)	126.4(8)	Ni(2)−N(19)−C(58)	129.8(9)

mL), water (2 times, 250 mL), and dried ($MgSO_4$). The solvent was removed by rotary evaporation to yield a yellow oil (crude 220 g, 90%) which was used without further purification: EI MS *m*/*e* 268 ($M^{\bullet+}$).

Dipropylfumaronitrile (2). This procedure is similar to that reported by Fitzgerald and co-workers for diethylfumaronitrile. A suspension of CuCN (156 g, 1.72 mol) in anhydrous DMF (1.5 L) was heated to 145 °C for approximately 1 h, or until the solution turned clear with some white solid adhered to the sides of the flask. The solution was cooled to 130 °C, and 4,5-dibromo-4*E*-octene (240 g, 0.88 mol) was added all at once. The solution turned dark brown, and heating with stirring was continued for at least 12 h but for no longer than 18 h. After this time the solution was allowed to cool to room temperature and carefully poured into concentrated ammonium hydroxide (2.5 L). The solution was stirred for approximately 30 min, and portions (500 mL) were extracted three times each with hexanes (500 mL). The large volume of hexanes was reduced to approximately 750 mL and washed once with water and once with brine to remove any residual DMF. The organic layer was dried ($MgSO_4$), and the solvent was removed by rotary evaporation. The resulting brown oil was purified by vacuum distillation to give a clear oil (93 g, 65%): ^{1}H NMR ($CDCl_3$) δ 0.98 (6H, t), 1.65 (4H, m), 2.54 (4H, t); ^{13}C NMR ($CDCl_3$) δ 12.4, 20.6, 35.0, 114.8, 128.5; EI MS *m*/*e* 162 ($M^{\bullet+}$).

2,3-Dipropylmaleonitrile (3). The fumaronitrile (50 g) was dissolved in acetonitrile (1 L) in a quartz round-bottom flask and sealed with a septum. Nitrogen was bubbled through the solution for a minimum of 20 min before the flask was placed in a Rayonet photochemical reactor fitted with a magnetic stirrer. The solution was irradiated with 253 nm (λ_{max}) light for 30 h, during which time the reaction temperature rose to approximately 40 °C from the heat given off by the reactor lamps. After approximately 30 h the reaction reached a photostationary state and was stopped. The solvent was removed by rotary evaporation, and the cis and trans isomers were separated by fractional distillation under high vacuum. The trans isomer distilled first, at about 40 °C lower than the desired cis isomer (22 g, 44% cis isolated): ^{1}H NMR ($CDCl_3$) δ 0.98 (6H, t), 1.64 (4H, m), 2.35 (4H, t); ^{13}C NMR ($CDCl_3$) δ 12.7, 20.5, 31.5, 115.9, 128.7; HR EI MS *m*/*e* 162.115 ($M^{\bullet+}$) (calcd for $C_{10}H_{14}N_2$: 162.116).

Mg[pz(NMe$_2$)$_2$(Pr)$_6$] (6). *N*,*N*,*N*′,*N*′-Tetramethyldiaminomaleonitrile (1.0 g, 6.0 mmol) and 2,3-dipropylmaleonitrile (7.0 g, 42 mmol) were added to a suspension of magnesium butoxide (from 300 mg of Mg°) in butanol (120 mL) heated at reflux. The solution turned yellow immediately, was brown after 15 min, and was a deep blue color after 45 min. The solution was heated at reflux for a period of 15 h, after which the reaction was cooled to 80 °C and the butanol removed by vacuum distillation. The resulting blue residue was taken up in chloroform (500 mL) and filtered. The solution was concentrated to 30 mL and subjected to flash silica gel chromatography (eluant: chloroform) to give the less polar octapropyl porphyrazine product, **5** (FAB MS *m*/*e* 673 $(M + H)^+$), being followed immediately by the desired hybrid porphyrazine: FAB MS *m*/*e* 675 $(M + H^{\bullet})^+$. This compound was carried on to the next step without further purification.

H$_2$[pz(NMe$_2$)$_2$(Pr)$_6$] (7). The Mg porphyrazine, **6**, was treated with CF_3CO_2H (enough to dissolve all of the porphyrazine, approximately 30−50 mL) for 15 min. After this time, the solution was poured over crushed ice and the flask was rinsed with water (200 mL). The ice slurry containing the blue precipitate was made basic by addition of concentrated aqueous NH_3 (to pH 10−12). The solid was collected by suction filtration and washed copiously with MeOH until the washings were clear. The pure product (780 mg, 19%) was obtained following column chromatography on silica gel (eluant: $CHCl_3$): ^{1}H NMR ($CDCl_3$) δ −1.77 (2H, N*H*, s), 1.26 (18H, t), 2.30 (12H, m), 3.85 (12H, t), 3.89 (12H, s); λ_{max} (nm) 338, 554, 630; FAB$^+$ MS *m*/*e* 652 ($M^{\bullet+}$). Anal. Calcd for $C_{38}H_{56}N_{10}$: C, 69.90; H, 8.64; N, 21.45. Found: C, 69.44; H, 8.53; N, 21.41.

Ni[pz(NMe$_2$)$_2$(Pr)$_6$] (8). Freebase porphyrazine, **7**, (780 mg, 1.17 mmol) and nickel(II) acetate tetrahyrdate (290 mg, 1.17 mmol) in a mixture of chlorobenzene (50 mL) and DMF (15 mL) were heated to 100 °C for 18 h, after which the solvent was removed by vacuum distillation. The blue residue was taken up in $CHCl_3$ (250 mL) and filtered. The volume was reduced to 30 mL by rotary evaporation, and the product (800 mg, 95%) was purfied by silica gel chromatography (eluant: $CHCl_3$) and washing the resulting solid with copious amounts of hexanes, diethyl ether, and finally methanol: ^{1}H NMR ($CDCl_3$) δ 1.24 (18H, m), 2.22 (12H, m), 3.69 (12H, t), 3.85 (12H, s); λ_{max} (nm) 319, 577; FAB$^+$ MS *m*/*e* 708 $(M + H)^+$. Anal. Calcd for $C_{38}H_{54}N_{10}Ni{\cdot}CH_3OH$: C, 63.16; H, 7.88; N, 18.89. Found: C, 63.61; H, 7.68; N, 18.68.

Cu[pz(NMe$_2$)$_2$(Pr)$_6$] (9). Freebase porphyrazine, **7**, (500 mg, 0.767 mmol) and copper(II) acetate (0.140 g, 0.767 mmol) in $CHCl_3$ (50 mL) and MeCN (15 mL) were heated to 50 °C for 2 h, after which the solvent was removed by rotary evaporation. The blue residue was taken up in $CHCl_3$ (250 mL) and filtered. The volume was reduced to 30 mL by rotary evaporation and the product (510 mg, 93%) was purfied by silica gel chromatography (eluant: $CHCl_3$): λ_{max} (nm) 341, 579; FAB$^+$ MS *m*/*e* 713 ($M^{\bullet+}$). Anal. Calcd for $C_{38}H_{54}CuN_{10}$: C, 63.88; H, 7.62; N, 19.60. Found: C, 63.61; H, 7.51; N, 18.89.

Mn^{III}[pz(NMe$_2$)$_2$(Pr)$_6$]$^+$[Cl$^-$] (10). Freebase porphyrazine, **7** (475 mg, 0.73 mmol), manganese(II) chloride tetrahydrate (1 g, 5.08 mmol) in chlorobenzene (90 mL) and DMF (30 mL) were heated to 100 °C for 18 h after which the solvent was removed by vacuum distillation. The blue residue was taken up in $CHCl_3$ (250 mL) and filtered. The pure product (460 mg, 86%) was obtained following column chromatography on silica gel (eluant: 2% MeOH in $CHCl_3$): λ_{max} (nm) 364, 594, 622; FAB$^+$ MS *m*/*e* 740 ($M^{\bullet+}$), 705 $(M - Cl)^+$. Anal. Calcd for $C_{38}H_{54}ClMn\ N_{10}$: C, 61.57; H, 7.34; N, 18.89; Cl, 4.78. Found: C, 61.56; H, 7.42; N, 18.73; Cl, 5.00.

Ni[pz(NMe$_2$)$_2$(Pr)$_6$]PdCl$_2$ (11). Compound **8** (300 mg, 0.42 mmol) and palladium(II) chloride (74 mg, 0.42 mmol) in a mixture of $CHCl_3$ (30 mL) and MeCN (10 mL) were heated to reflux. During the course of the reaction the color of the solution changed from blue to purple. The reaction was monitored by thin-layer chromatography and was stopped after no starting porphyrazine remained (about 3 h). The solvent was removed by rotary evaporation, and the resulting product (350 mg, 95%) was purified by chromatography on silica gel (eluant:

Table 4. Postional Parameters and *B*(eq) for **13**

atom	*x*	*y*	*z*	*B*(eq)	atom	*x*	*y*	*z*	*B*(eq)
Pd(1)	0.03716(7)	0.62654(6)	0.01671(4)	2.21(3)	C(28)	−0.4282(9)	0.5047(8)	0.3335(5)	4.6(5)
Pd(2)	−0.26851(7)	0.73560(5)	0.23119(4)	2.23(3)	C(29)	−0.4406(8)	0.5357(8)	0.1333(5)	4.0(4)
Ni(1)	−0.1165(1)	0.54292(9)	0.19658(6)	1.91(4)	C(30)	−0.474(1)	0.4591(9)	0.1231(7)	8.0(7)
Ni(2)	−0.4017(1)	0.68587(8)	0.42131(6)	2.14(4)	C(31)	−0.562(1)	0.457(1)	0.1255(9)	12.1(9)
Cl(1)	0.9394(3)	0.2677(3)	0.7101(2)	9.7(2)	C(32)	−0.3664(8)	0.5840(8)	0.0495(5)	4.2(4)
Cl(2)	0.8683(4)	0.1968(5)	0.7715(2)	15.8(3)	C(33)	−0.354(1)	0.5226(10)	0.0132(6)	6.1(6)
Cl(3)	0.9801(4)	0.1245(3)	0.7358(4)	21.0(4)	C(34a)	−0.375(3)	0.531(3)	−0.029(2)	5(1)
S(1)	−0.0159(2)	0.6254(2)	−0.0584(1)	2.86(10)	C(34b)	−0.403(1)	0.459(1)	0.0123(8)	5.2(6)
S(2)	0.1587(2)	0.6389(2)	0.0041(1)	2.75(10)	C(35)	−0.1180(8)	0.6937(7)	0.0207(4)	3.0(4)
S(3)	−0.3270(2)	0.7445(2)	0.1574(1)	2.75(10)	C(36)	−0.1288(8)	0.5611(7)	0.0015(5)	3.1(4)
S(4)	−0.1500(2)	0.7329(2)	0.2156(1)	2.60(9)	C(37)	0.1185(8)	0.6899(7)	0.1079(4)	3.0(4)
N(1)	−0.0743(6)	0.5732(5)	0.1480(3)	1.7(3)	C(38)	0.1412(7)	0.5568(7)	0.1006(4)	2.7(4)
N(2)	0.0659(6)	0.5795(5)	0.1850(3)	1.9(3)	C(39)	0.1408(8)	0.6290(7)	−0.0543(5)	2.4(4)
N(3)	−0.0172(6)	0.5414(5)	0.2355(3)	1.7(3)	C(40)	0.0715(9)	0.6236(7)	−0.0802(5)	2.7(4)
N(4)	−0.0395(6)	0.4979(5)	0.3046(3)	2.1(3)	C(41)	0.2088(9)	0.6274(7)	−0.0740(4)	2.9(4)
N(5)	−0.1588(6)	0.5106(5)	0.2450(3)	1.9(3)	C(42)	0.0514(9)	0.6148(6)	−0.1297(5)	2.8(4)
N(6)	−0.2988(6)	0.5098(6)	0.2090(4)	2.1(3)	C(43)	−0.4092(9)	0.7145(6)	0.3268(5)	2.6(4)
N(7)	−0.2179(6)	0.5462(5)	0.1585(3)	1.8(3)	C(44)	−0.3580(8)	0.7247(6)	0.2953(5)	1.9(3)
N(8)	−0.1940(6)	0.5819(5)	0.0880(3)	2.1(3)	C(45)	−0.2867(8)	0.7203(6)	0.3198(4)	1.7(3)
N(9)	−0.0772(6)	0.6184(5)	0.0302(3)	2.1(3)	C(46)	−0.2867(8)	0.7066(6)	0.3665(4)	1.7(3)
N(10)	0.0821(6)	0.6178(5)	0.0885(3)	1.9(3)	C(47)	−0.2280(8)	0.6879(6)	0.4433(5)	2.3(4)
N(11)	0.0397(8)	0.6077(6)	−0.1675(4)	4.6(4)	C(48)	−0.1593(8)	0.6817(6)	0.4800(4)	2.1(3)
N(12)	0.2594(8)	0.6248(6)	−0.0910(4)	4.4(4)	C(49)	−0.1854(9)	0.6709(6)	0.5178(5)	2.4(4)
N(13)	−0.3635(7)	0.7034(5)	0.3691(4)	2.1(3)	C(50)	−0.2700(9)	0.6692(7)	0.5018(5)	2.5(4)
N(14)	−0.2227(6)	0.6993(5)	0.4009(3)	1.7(3)	C(51)	−0.3927(9)	0.6500(7)	0.5151(5)	2.7(4)
N(15)	−0.2985(6)	0.6807(5)	0.4575(4)	2.1(3)	C(52)	−0.4450(8)	0.6286(7)	0.5454(5)	2.3(4)
N(16)	−0.3155(7)	0.6531(5)	0.5306(4)	2.5(3)	C(53)	−0.5197(9)	0.6336(7)	0.5198(5)	2.3(4)
N(17)	−0.4408(7)	0.6650(5)	0.4724(3)	2.1(3)	C(54)	−0.5174(9)	0.6572(6)	0.4742(4)	1.8(4)
N(18)	−0.5805(7)	0.6700(5)	0.4419(4)	2.2(3)	C(55)	−0.5723(8)	0.6892(6)	0.4020(5)	2.2(4)
N(19)	−0.5047(6)	0.6944(5)	0.3866(4)	1.9(3)	C(56)	−0.6419(8)	0.7071(6)	0.3654(5)	2.4(4)
N(20)	−0.4877(7)	0.7173(5)	0.3125(4)	2.2(3)	C(57)	−0.6147(8)	0.7188(6)	0.3277(4)	2.2(4)
N(21)	−0.3804(6)	0.7376(6)	0.2478(3)	2.1(3)	C(58)	−0.5313(8)	0.7093(6)	0.3426(5)	2.3(4)
N(22)	−0.2161(6)	0.7316(5)	0.3020(3)	2.0(3)	C(59)	−0.0786(8)	0.6871(7)	0.4743(4)	3.2(4)
N(23)	−0.2833(7)	0.7833(6)	0.0468(4)	3.7(3)	C(60)	−0.0506(8)	0.7654(8)	0.4660(5)	3.8(4)
N(24)	−0.0482(7)	0.7702(6)	0.1276(3)	2.9(3)	C(61)	0.0293(10)	0.7665(9)	0.4545(6)	6.3(5)
C(1)	−0.1158(8)	0.5842(6)	0.1048(5)	2.1(4)	C(62)	−0.1409(8)	0.6569(7)	0.5649(5)	3.4(4)
C(2)	−0.0593(8)	0.6018(6)	0.0771(4)	1.6(3)	C(63a)	−0.144(2)	0.725(2)	0.595(1)	5.5(8)
C(3)	0.0112(8)	0.6017(6)	0.1043(4)	1.8(3)	C(63b)	−0.089(2)	0.725(2)	0.591(1)	5.6(9)
C(4)	0.0038(8)	0.5840(6)	0.1491(4)	1.8(3)	C(64b)	−0.154(2)	0.788(2)	0.594(1)	6.6(10)
C(5)	0.0537(8)	0.5602(6)	0.2249(4)	2.2(4)	C(64a)	−0.109(3)	0.789(2)	0.582(1)	7(1)
C(6)	0.1214(8)	0.5551(6)	0.2633(4)	1.9(3)	C(65)	−0.4141(8)	0.6075(7)	0.5928(4)	2.8(4)
C(7)	0.0909(8)	0.5315(6)	0.2977(5)	2.2(3)	C(66)	−0.3965(9)	0.5237(7)	0.5984(5)	4.1(4)
C(8)	0.0084(8)	0.5232(6)	0.2789(4)	2.1(3)	C(67)	−0.3671(8)	0.5034(7)	0.6471(5)	4.0(4)
C(9)	−0.1161(8)	0.4928(6)	0.2870(5)	2.1(4)	C(68)	−0.5950(8)	0.6156(7)	0.5319(4)	2.6(4)
C(10)	−0.1710(8)	0.4675(6)	0.3143(5)	2.2(4)	C(69)	−0.6247(9)	0.5362(7)	0.5243(5)	4.2(4)
C(11)	−0.2420(8)	0.4722(7)	0.2876(5)	2.1(4)	C(70)	−0.7006(9)	0.5227(7)	0.5389(5)	4.8(5)
C(12)	−0.2381(9)	0.4991(7)	0.2428(5)	2.5(4)	C(71)	−0.7259(8)	0.7075(7)	0.3699(5)	3.7(4)
C(13)	−0.2903(8)	0.5322(7)	0.1694(5)	2.2(4)	C(72)	−0.7477(10)	0.778(1)	0.3937(6)	6.0(6)
C(14)	−0.3571(8)	0.5435(7)	0.1313(5)	2.6(4)	C(73)	−0.743(1)	0.849(1)	0.3687(7)	8.7(7)
C(15)	−0.3265(8)	0.5630(7)	0.0963(5)	2.5(4)	C(74)	−0.6574(8)	0.7356(7)	0.2803(4)	3.2(4)
C(16)	−0.2418(8)	0.5637(7)	0.1162(5)	2.3(4)	C(75)	−0.6463(8)	0.8156(7)	0.2658(5)	3.7(4)
C(17)	0.2035(8)	0.5733(7)	0.2605(4)	3.2(4)	C(76)	−0.6704(10)	0.8254(8)	0.2149(5)	5.5(5)
C(18)	0.2417(8)	0.5116(7)	0.2379(4)	2.9(4)	C(77)	−0.4320(8)	0.6776(7)	0.2243(4)	3.2(4)
C(19)	0.3182(8)	0.5375(8)	0.2258(5)	4.9(5)	C(78)	−0.4178(8)	0.8123(7)	0.2390(4)	3.1(4)
C(20)	0.1309(8)	0.5191(7)	0.3460(4)	2.9(4)	C(79)	−0.1781(8)	0.8044(7)	0.3176(4)	2.8(4)
C(21)	0.1094(8)	0.5779(7)	0.3774(4)	2.8(4)	C(80)	−0.1571(8)	0.6712(7)	0.3151(5)	3.2(4)
C(22)	0.1516(9)	0.5659(8)	0.4266(5)	4.7(5)	C(81)	−0.2475(8)	0.7560(7)	0.1329(4)	2.4(4)
C(23)	−0.1422(8)	0.4428(7)	0.3620(5)	2.9(4)	C(82)	−0.1728(8)	0.7492(7)	0.1579(4)	2.2(4)
C(24)	−0.1194(8)	0.5056(7)	0.3965(5)	3.3(4)	C(83)	−0.2661(8)	0.7705(7)	0.0854(5)	2.6(4)
C(25)	−0.0842(9)	0.4774(8)	0.4450(5)	4.3(4)	C(84)	−0.1048(8)	0.7612(7)	0.1400(4)	2.0(3)
C(26)	−0.3211(8)	0.4553(7)	0.2984(5)	3.4(4)	C(85)	0.955(1)	0.208(1)	0.7537(6)	7.2(6)
C(27)	−0.3483(8)	0.5189(7)	0.3238(5)	3.6(4)					

$CHCl_3$): ^{1}H NMR ($CDCl_3$) δ 1.25 (18H, m), 2.23 (12H, m), 3.67 (12H, m), 4.18 (12H, s); λ_{max} (nm) 322, 338 (sh), 575, 600; FAB^+ MS *m*/*e* 708 $(M - PdCl_2)^+$. Anal. Calcd for $C_{38}H_{54}Cl_2N_{10}NiPd$: C, 51.46; H, 6.14; N, 15.79. Found: C, 51.69; H, 6.17; N, 15.81.

Cu[pz(NMe$_2$)$_2$(Pr)$_6$]PdCl$_2$ (12). This compound was prepared from **9** by the same procedure described for **11** above: FAB^+ MS *m*/*e* 819 (M − 2Cl), 714 (M − $PdCl_2$. Anal. Calcd for $C_{38}H_{54}Cl_2CuN_{10}Pd$: C, 51.18; H, 6.10; N, 15.71. Found: C, 51.01; H, 6.11; N, 15.50.

Ni[pz(NMe$_2$)$_2$(Pr)$_6$]Pd(mnt) (13). Na_2MNT (5.2 mg, 2.8×10^{-2} mmol) in MeOH (3 mL) was added dropwise over a 15 min to a rapidly stirring solution of **11** (25 mg, 2.8×10^{-2} mmol) in $CHCl_3$/MeOH (3/1; 8 mL) in an ice bath when thin-layer chromatography revealed the appearance of 2 new products. The lead spot, moving with the solvent ($CHCl_3$) front ($R_f = 1.0$) was determined to be **8**. After stirring for 1 h at 0 °C the solution was warmed to room temperature and the solvent removed by rotary evaporation. The second product seen on the TLC plate was isolated pure (16 mg, 61%) following chromatography on silica gel (eluant: $CHCl_3$). Crystals suitable for X-ray diffraction were grown by slow diffusion of MeOH into a $CHCl_3$ solution of the product: ^{1}H NMR ($CDCl_3$) δ 1.24 (18H, m), 2.25 (12H,

m), 3.75 (12H, m), 4.21 (12H, s); λ_{max} (nm) 321, 340 (sh), 576, 601; IR ν_{CN} 2200 cm^{-1}; FAB^+ MS *m/e* 956 (M + H). Anal. Calcd for $C_{42}H_{54}N_{12}NiPdS_2$: C, 52.76; H, 5.69; N, 17.58. Found: C, 52.72; H, 5.63; N, 17.37.

Ni[pz(NMe$_2$)$_2$(Pr)$_6$]Pd(bdt) (14). A solution of Na_2BDT (6.3 mg, 3.37×10^{-2} mmol) in MeOH (10 mL) was added dropwise by cannula to **11** (30 mg, 3.37×10^{-2} mmol) in $CHCl_3$ (30 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 1 h, after which time the solvent was evaporated under reduced pressure. Thin-layer chromatography revealed a new product moving just ahead of the starting porphyrazine, **11**, and this was isolated pure (17 mg, 52%) following silica gel chromatography (eluant: $CHCl_3$): ^1H NMR ($CDCl_3$) δ 1.25 (18H, m), 2.23 (12H, m), 3.64 (4H, t), 3.75 (8H, m), 4.27 (12H, s), 6.90 (2H, m), 7.24 (2H, m); FAB^+ MS *m/e* 956 $(M + H)^+$. Anal. Calcd for $C_{44}H_{58}N_{10}NiPdS_2$: C, 55.27; H, 6.11; N, 14.65. Found: C, 54.76; H, 6.06; N, 14.39.

Ni[pz(NMe$_2$)$_2$(Pr)$_6$]Pd(dmid) (15). Sodium metal (10 mg, 0.45 mmol) was added to a suspension of 1,3,4,6-tetrathiapentalene-2,5-dione (24 mg, 0.13 mmol) in dry and degassed MeOH (8 mL) under nitrogen. The yellow solution that formed was stirred at room temperature for 2 h; the solution was then cooled to 0 °C, and **11** (100 mg, 0.11 mmol) in degassed $CHCl_3$ (40 mL) was added dropwise by cannula. The solvent was removed under reduced pressure at 0 °C, and the pure product (76 mg, 70%) was obtained following column chromatography on silica gel (eluant: $CHCl_3$): ^1H NMR ($CDCl_3$) δ 1.28 (18H, m), 2.25 (12H, m), 3.78 (12H, m), 4.29 (12H, s); FAB^+ MS *m/e* 995 ($M^{\bullet+}$). Anal. Calcd for $C_{41}H_{54}N_{10}NiOPdS_4$: C, 49.43; H, 5.46; N, 14.06. Found: C, 49.30; H, 5.46; N, 14.02.

(Ni[pz(NMe$_2$)$_2$(Pr)$_6$]Pd)$_2$(btt) (16). Sodium metal (20 mg, 0.87 mmol) was added to a suspension of 1,2,4,5-tetra(benzylthio)benzene in liquid ammonia at −78 °C under nitrogen. The solution turned deep blue in color, was stirred for 1 h, and was then allowed to warm slowly to reflux (−33 °C). After an additional 30 min, the mixture was cooled to −78 °C and quenched with NH_4Cl (23 mg) to leave a white suspension. The cold bath was removed, the ammonia allowed to boil off under a stream of dry nitrogen gas, and the white residue was dissolved in degassed MeOH (10 mL) and added dropwise by cannula to a solution of **11** (100 mg, 0.11 mmol) in $CHCl_3$/MeOH (3/1; 20 mL) at 0 °C. After addition of the tetrathiolate solution was complete, the mixture was stirred for an additional 20 min and filtered cold. The solid residue formed a dilute solution in cold (approximately 0 °C) chloroform and was quickly chromatographed on a chilled silica gel column (eluant: $CHCl_3$). The elution of **8** from the column prior to the product was evidence for some further disproportionation on the column material. The product was collected in a chilled flask and the solvent was pumped off under high vacuum. Thin-layer chromatography of the product showed a single spot: FAB^+ MS *m/e* 1832 $(M + H)^+$; the room-temperature proton NMR spectrum showed a mixture of overlapped product peaks and those of **8**. ^1H NMR ($CDCl_3$) δ 1.26 (m, $-CH_2CH_2CH_3$, from **8** and **16**), 2.24 (m, $-CH_2CH_2CH_3$, from **8** and **16**), 3.73 (m, $-CH_2CH_2CH_3$, from **8** and **16**), 3.85 (s, $N(CH_3)_2$, from **8**), 4.26 (s, $N(CH_3)_2$, from **16**), 7.54 (s, *Ar*). The product disproportionates rapidly in concentrated solution and this instability precluded further characterization.

(Cu[pz(NMe$_2$)$_2$(Pr)$_6$]Pd)$_2$(btt) (17). This compound was prepared from **12** by the same procedure described for **16**: FAB^+ MS *m/e* cluster 1841−1846 ($(M + H)^+ = 1841$), 1130 (M − Cu[pz(NMe$_2$)$_2$(Pr)$_6$]). The instability of the product prevented further characterization.

Ni[pz(NMe$_2$)$_2$(Pr)$_6$]PtCl$_2$ (18). Dichlorobis(benzonitrile)platinum(II) (480 mg, 0.879 mmol) and **8** (620 mg, 0.879 mmol) were added to 1,2-dichloroethane (250 mL) and heated at reflux with stirring under nitrogen. The course of the reaction was monitored by thin-layer chromatography, and after a period of 18−24 h only a small amount of **8** remained and the reaction was stopped. The solvent was removed by rotary evaporation, and the pure product (615 mg, 72%) was obtained following column chromatography on silica gel (eluant, $CHCl_3$); alternatively, **18** can be crystallized by layered diffusion of MeOH into a solution of the complex in $CHCl_3$: ^1H NMR ($CDCl_3$) δ 1.25 (18H, m), 2.22 (12H, m), 3.64 (4H, m), 3.73 (8H, m), 4.35 (12H, s); λ_{max} (nm) 320, 338 (sh), 575, 600; FAB^+ MS *m/e* 975 $(M + H)^+$, 940 $(M - Cl)^+$. Anal. Calcd for $C_{38}H_{54}Cl_2N_{10}NiPt\cdot CHCl_3$: C, 42.78; H, 5.06; N, 12.79. Found: C, 43.39; H, 5.11; N, 12.98.

Cu[pz(NMe$_2$)$_2$(Pr)$_6$]PtCl$_2$ (19). This compound was prepared and purified by the same procedures described for **18** above: λ_{max} (nm) 341, 572, 600; FAB^+ MS *m/e* 944 $(M - Cl)^+$, 906 $(M - 2Cl)^+$, 713 $(M - PtCl_2)^+$. Anal. Calcd for $C_{38}H_{54}N_{10}Cl_2CuPt\cdot CHCl_3$: C, 42.59; H, 5.04; N, 12.74. Found: C, 42.59; H, 5.07; N, 12.80.

Dibutyltin-3,4-toluenedithiolate (20). 3,4-Toluenedithiol (2.00 g, 13 mmol), dibutyltin dichloride (3.89 g, 13 mmol), and triethylamine (4 mL) were added to degassed MeOH (50 mL) under nitrogen, and the mixture was stirred at room-temperature overnight. The solvent was removed by rotary evaporation, and the residue was taken up in $CHCl_3$ (100 mL) and filtered. The pure product (4.1 g, 81%) was obtained as a clear oil following column chromatography on silica gel (eluant: $CHCl_3$/hexanes, 1/1): ^1H NMR ($CDCl_3$) δ 0.93 (6H, t), 1.38 (4H, m), 1.65 (4H, m), 1.75 (4H, m), 2.23 (3H, s), 6.71 (1H, 4 lines), 7.32 (2H, 3 lines); ^{13}C NMR ($CDCl_3$) δ 13.4, 20.4, 21.7, 26.5, 27.7, 125.1, 129.5, 130.2, 133.7, 134.4, 137.9; FAB^+ MS *m/e* 389 $(M + H)^+$. The tin derivative was used directly without any further purification.

Ni[pz(NMe$_2$)$_2$(Pr)$_6$]Pt(tdt) (21). Dibutyltin(tdt), **20**, (100 mg, 0.257 mmol) and **16** (200 mg, 0.205 mmol) were added to 1,2-dichloroethane (20 mL) and heated at 70 °C with stirring under nitrogen. The course of the reaction was monitored by thin-layer chromatography. The presence of free ligand, **8**, on the TLC plate after a period of 4−6 h indicated that some product was being lost to the competing disproportionation bis(tdt)Pt^{II} reaction. To prevent further product loss, the reaction was stopped at this time and the solvent removed by rotary evaporation. The pure product (65 mg, 30%) was obtained following purification by column chromatography on silica gel (eluant: $CHCl_3$); an additional amount (50 mg) of starting material **18** was recovered as a slower moving product: ^1H NMR ($CDCl_3$) δ 1.26 (18H, t), 2.24 (12H, m), 2.28 (3H, s), 3.77 (12H, m), 4.52 (12H, s), 6.65 (1H, 4 lines), 7.27 (2H, m); FAB^+ MS *m/e* 1058 ($M^{\bullet+}$).

Ni[pz(NMe$_2$)$_2$(Pr)$_6$]Pt(dmit) (22). Dibutyltin(dmit)[8,9] (27 mg, 0.051 mmol) and **18** (50 mg, 0.051 mmol) were added to 1,2-dichloroethane (10 mL) and heated at reflux with stirring under nitrogen. The reaction was stopped after a period of 3−4 h when **18** was no longer observed by TLC. The pure product (36 mg, 64%) was obtained following column chromatography on silica gel (eluant $CHCl_3$): ^1H NMR ($CDCl_3$) δ 1.26 (18H, m), 2.25 (12H, m), 3.75 (12H, m), 4.50 (12H, s); FAB^+ MS *m/e* 1100 $(M + H)^+$. Anal. Calcd for $C_{41}H_{54}N_{10}NiPtS_5$: C, 44.73; H, 4.94; N, 12.72. Found: C, 44.45; H, 4.94; N, 12.25.

Results and Discussion

Macrocycle Synthesis. Fully symmetric porphyrazines ($\mathbf{A}_4$ or $\mathbf{B}_4$) can be synthesized by the magnesium template cyclization of a single maleonitrile derivative in hot magnesium alkoxide.[10] Porphyrazines having differing peripheral substitutents are prepared by co-cyclizing two different maleonitrile derivatives.[11−13] When stoichiometric amounts (3:1) are used, a mixture of all six possible porphyrazine products is often obtained, and separation of the desired singly substituted $\mathbf{AB}_3$ product by standard column chromatographic techniques can be very difficult. However, we have shown[14] that when one of the maleonitrile derivatives is present in excess, only two porphyrinic products are obtained: the fully symmetric $\mathbf{B}_4$ porphyrazine, and the desired $\mathbf{AB}_3$ porphyrazine. When **A** contains

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heteroatoms and **B** is composed of alkyl groups, the $\mathbf{AB}_3$ and $\mathbf{B}_4$ prophyrazines are easily purified by silica gel chromatography.

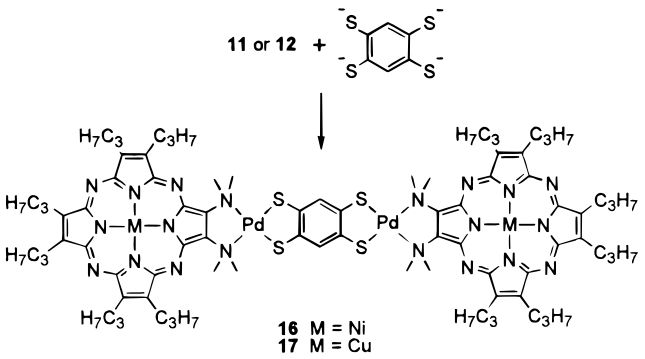
To achieve reasonable yields of the unsymmetrical porphyrazine, the **A** and **B** maleonitriles also must have compatible cyclization rates. If one component reacts significantly faster than the other, it will be consumed to form predominantly the fully symmetric $\mathbf{A}_4$ or $\mathbf{B}_4$ product, and only very small amounts of the component that cyclizes more slowly will be incorporated into mixed products. In general, we find that maleonitrile derivatives substituted with electron withdrawing groups tend to cyclize more rapidly than those substituted with donating groups. To optimize the yield of the $\mathbf{AB}_3$ porphyrazine substituted with one **A** = bis(dimethylamino) chelate, four **B** dinitrile derivatives were investigated for co-cyclization with bis(dimethylamino)maleonitrile (tmdamn).[15] Of those investigated only dipropyl maleonitrile proved suitable for this study.

Dipropyl maleonitrile, **3**, has appropriate reactivity for co-cyclization with tmdamn and can be conveniently prepared in 50−75 g quantities following minor modification of Fitzgerald's procedure for diethyl maleonitrile.[16,17] As outlined in Scheme 1, co-cyclization of **3** with tmdamn, **4**, in a suspension of magnesium butoxide in refluxing butanol produced unsymmetrical porphyrazine **6**, $Mg[pz(NMe_2)_2(Pr)_6]$, and magnesium octapropyl porphyrazine, **5**. Both **5** and **6** are freely soluble in halogenated solvents and are easily separated from the reaction mixture by passage through one silica gel column. The magnesium(II) ion is removed by treatment with trifluoroacetic acid to give the freebase compound **7**. Reaction of **7** with 1 equiv of $Ni(OAc)_2 \cdot 4H_2O$ in a mixture of DMF and chlorobenzene at 90 °C proceeds smoothly to give the centrally metalated product **8**, without peripheral metalation. The Cu(II) porphyrazine, **9**, was obtained after reaction of **7** with 1 equiv of $Cu(OAc)_2$ in chloroform/acetonitrile (3/1) at 50 °C. Manganese(II) also incorporates into the macrocyclic cavity **10**, oxidizing to Mn(III) during the reaction.[18]

Peripheral Metalation. When **7** is treated with excess Ni(II), the resulting product does not move in thin-layer chromatography but gives **8** when reacted with disodium maleonitriledithiolate (Na_2mnt). Clearly peripheral metalation by the dimethylamino chelate also occurs in the presence of excess Ni(II) ion, but this ion is stripped from the ligand by reaction with mnt^{2-}.

Reaction of **8** or **9** with 1 equiv of $PdCl_2$ in a chloroform/acetonitrile solution (3/1) at reflux, gives the bimetallic porphyrazines with peripherally coordinated $PdCl_2$, **11** and **12**, respectively (Scheme 1). The chloride ions of **11** are displaced by reaction with the dithiolene chelates, maleonitriledithiolate (mnt^{2-}), benzenedithiolate (bdt^{2-}), and 1,3-dithiole-2-one-4,5-dithiolate ($dmid^{2-}$), to give the $[N_2-Pd-S_2]$-capped porphyrazines **13**, **14**, and **15**, respectively. An undesirable side reaction that occurs during the dithiolene capping reactions is disproportionation that leads to the formation of bis(dithiolene) palladium complexes, with concomitant regeneration of **8**. This process can be minimized by working at reduced temperatures (0 °C or colder) and slowly adding the dithiolate solution to the $PdCl_2$ porphyrazine solution. The uncharged Pd(II) dithiolene-capped compounds are easily purified by column chromatography on silica gel. The mnt^{2-}-capped porphyrazine, **13**, is stable in chloroform at elevated temperatures. However, the bdt^{2-}- and $dmid^{2-}$-capped complexes (**14** and **15**) disproportionate in chloroform over time to give $[bis(bdt)Pd]^{2-}$ and $[bis(dmid)Pd]^{2-}$, respectively, and ligand **8**.

Scheme 2



Reaction of 2 equiv of **11** or **12** with 1,2,4,5-benzenetetrathiolate (btt^{2-}), produced by reductive debenzylation of 1,2,4,5-tetrathiobenzylbenzene with sodium metal in liquid ammonia, gave the bis(Pd)(btt)-bridged porphyrazine dimers **16** and **17**, respectively (Scheme 2). Both products were purified by column chromatography and gave FAB^+ mass spectra consistent with this formulation. Unfortunately, **16** and **17** disproportionate rapidly in concentrated solution at room temperature and are insoluble at colder temperatures where they may exist for longer periods of time. This instability has thus far prevented further characterization and studies of these novel porphyrazine dimers.

To reduce the tendency of these dithiolene capped porphyrazines to disproportionate, we sought to replace the Pd(II) ion with the more substitutionally inert Pt(II).[19] Thus, the $PtCl_2$ adducts **18** and **19** were prepared by reaction of bis(benzonitrile)platinum(II) dichloride with **8** or **9** in 1,2-dichloroethane at refluxing temperatures for several hours. Of the many solvent systems investigated for this reaction, reasonable yields were obtained only with 1,2-dichloroethane. The $PtCl_2$ complexes are kinetically inert to chloride substitution and **18** reacts slowly and incompletely with Na_2mnt and Na_2bdt even at temperatures up to 90 °C. The sluggishness of these reactions led us to prepare a more reactive $Pt(OTf)_2$ porphyrazine adduct by treatment of **18** with AgOTf. Unfortunately the $Pt(OTf)_2$ complex of the porphyrazine reacted with Na_2bdt to give predominately the $[bis(bdt)Pt]^{2-}$ complex with recovery of ligand **8** and produced little of the desired $[N_2-Pt-S_2]$-capped porphyrazine.

This difficulty led us to develop an alternative method for the generation of heteroleptic $[N_2-Pt-S_2]$ complexes through the use of dialkyltin protected dithiolates as capping reagents. Complex **18** reacts with dibutyltin(toluene-3,4-dithiolate), **20**,

(15) The four dinitrile derivatives investigated are phthalonitrile (its $\mathbf{AB}_3$ product lacked sufficient solubility for this study); dibutylphthalonitrile (its $\mathbf{AB}_3$ product is soluble, however the synthesis of dibutylphthalonitrile proved inconvenient); bis(4-(*tert*-butyl)phenyl)pyrroline (formation of the $\mathbf{AB}_3$ product was not observed); and dipropyl maleonitrile (see text).

(16) Fitzgerald, J.; Taylor, W.; Owen, H. *Synthesis* **1991**, 686−688.

(17) Fitzgerald and co-workers recently reported octaethyl porphyrazine synthesized from diethyl maleonitrile. We now have synthesized dipropyl maleonitrile by a slight modification of the Fitzgerald procedure. Fitzgerald reports reaching a photostationary state with 50% conversion of the fumaro- to the maleonitrile after 72 h of irradiation with light from a medium pressure mercury lamp. We have achieved the same conversion in approximately 24 h in a Rayonet photochemical reactor fitted with 253 nm (λ_{max}) lamps. The cis and trans isomers are separated by fractional distillation (cis boils approximately 40 °C higher than trans), and the trans compound is then recycled.

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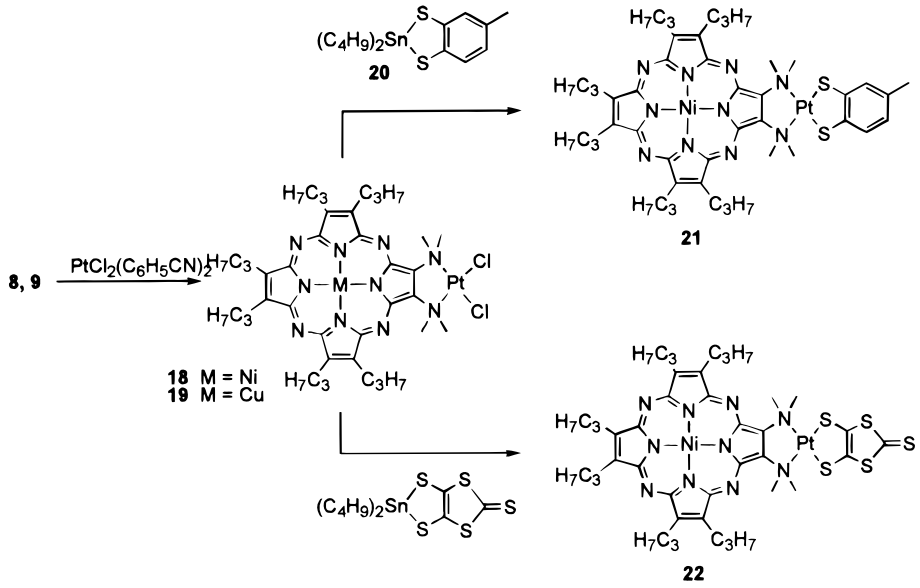
(19) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; John Wiley & Sons: New York, 1988; p 1297.

Scheme 3



or dibutyltin(dmit), in 1,2-dichloroethane at 80 °C to give the $[N_2-Pt-S_2]$-capped porphyrazines **21** and **22**, respectively (Scheme 3). The products were purified by silica gel chromatography. Both **21** and **22** are stable and do not undergo disproportionation in room temperature chloroform solutions even after several days, and are indefinitely stable as solid materials.

X-ray Structure of Ni[pz(NMe$_2$)$_2$(Pr)$_6$]Pd(mnt), 13. There are several structurally characterized examples of heteroleptic bis(phosphine)(dithiolene)palladium(II) complexes,[20−23] but prior to this report, none of a dithiolene−diamine palladium(II) complex. In fact, to our knowledge, only two palladium(II) dithiolene complexes bearing nitrogen donating groups have been previously reported,[24,25] and the N donors in both of these complexes are of the diimine type.

Complex **13** crystallizes with two chemically identical but crystallographically independent macrocycles and one $CHCl_3$ solvent molecule per asymmetric unit (Figure 2). Both macrocycles display a slight saddle distortion with mean deviation from the least-squares plane of the 24 core atoms of 0.07 Å for molecule **A** and 0.09 Å for molecule **B** (Figure 2). The asymmetry at the periphery is apparent in the macrocyclic core of both molecules in that each is elongated slightly along its noncrystallographic C_2 axis ($N_{pyrrole}-N_{pyrrole} = 3.79$ Å parallel to C_2 axis and 3.71 Å perpendicular to C_2 axis for both molecules). The Ni(II) ion of each molecule lies in the least-squares planes defined by the inner pyrrolic nitrogen atoms. The Ni−N bond distances (1.84−1.90 Å) and angles (88.7−91.5°) compare to those reported for other nickel(II)tetraazaporphyrin complexes.[5,26−28] Interestingly, the two molecules are oriented such that the Ni atom of molecule **A** (Ni1) lies directly beneath the S4 atom of molecule **B** at a distance of 3.538(4) Å (Figure 3). This distance is longer than what is normally considered to be a bond.

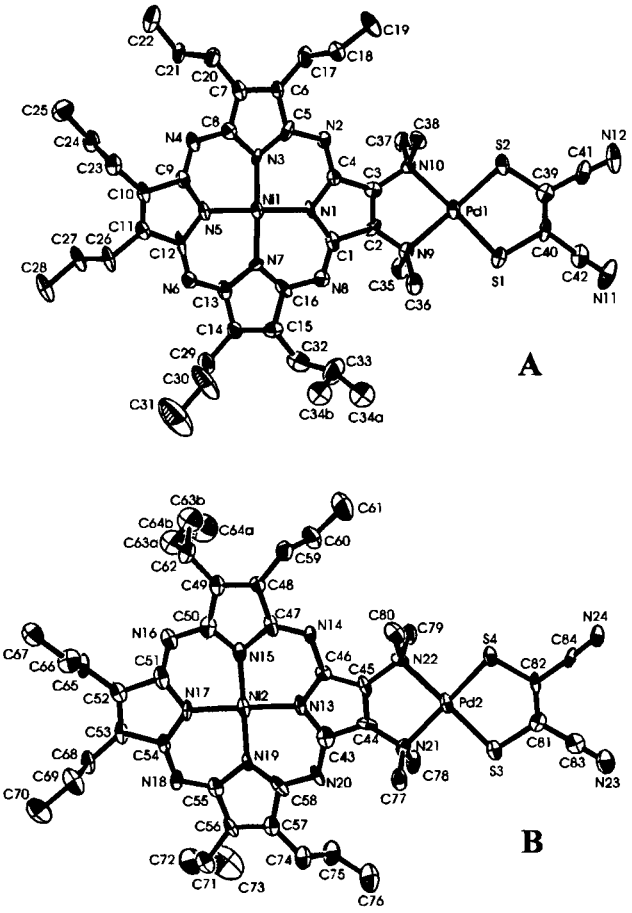


Figure 2. ORTEP representations of the crystallographically independent molecules of **13** with atom numbering scheme. Hydrogen atoms have been omitted for clarity.

(20) Ebihara, M.; Tsuchiya, M.; Kawamura, T. *Acta Crystallogr. C* **1994**, *50*, 1880.
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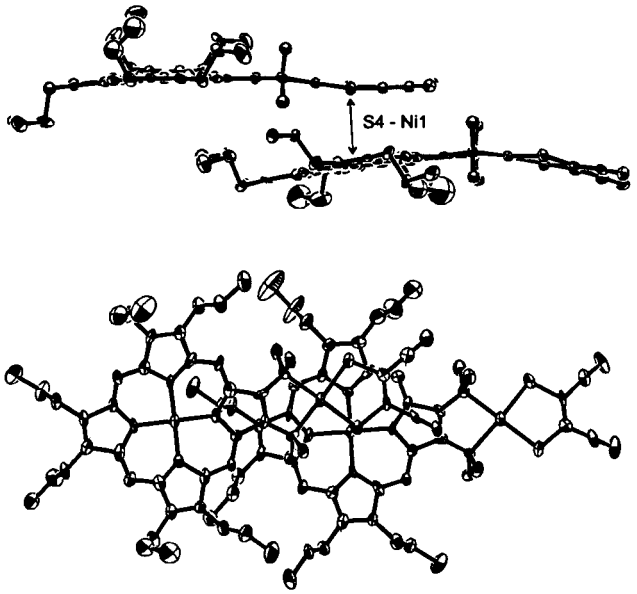

Figure 3. Side and top views of both molecules of **13**.

Both crystallographically independent Pd(II) ions in **13** are coordinated in an unsymmetrical square plane by two dimethylamino nitrogen atoms and the sulfur atoms of the maleonitrile dithiolate groups. The Pd−S (average Pd−S = 2.25 Å) and Pd−N (average Pd−N = 2.14 Å) bond distances (Table 2) compare to literature values for similar Pd−S[20−23] and Pd−N[29−31] bonds. The average intramolecular Ni−Pd separation for the two molecules is 6.85 Å.

UV−Visible Spectroscopy. The Cu(II) porphyrazine, **9**, exhibits an intense absorption in the Soret region at 322 nm (λ_{max}) and broad Q-band with λ_{max} at 588 nm (Figure 4, top). The spectrum of the freebase porphyrazine (**7**) is qualitatively similar, but with a split Q-band having Q_x and Q_y absorbances at 550 and 630 nm (Figure 4, middle). The splitting reflects the C_{2v} symmetry and can be rationalized by Gouterman's four orbital model for the optical spectra of porphyrins.[32] The Q-bands of both the freebase and metalated compounds are greatly broadened with respect to the Q-band of octapropylporphyrazine. This broadening is attributed to n-π^* transitions of the nonbonding electrons associated with the peripheral N atoms.

The porphrazines undergo a color change from blue to purple upon the peripheral coordination of metal ions to the dimethylamino chelate. The Q-band region sharpens greatly because the lone pair electrons on the $(NMe_2)_2$ moiety are datively bonded to the metal ions and thus their interactions with the porphyrazine ring are suppressed (Figure 4, bottom). Substitution of the chlorine ligands of **11** and **12** by the dithiolene ligands does not alter the UV−visible spectra further.

Electrochemistry. The electrochemical properties of the peripherally N-functionalized porphyrazines were studied by cyclic voltammetry in dichloromethane. The fully alkyl-substituted porphyrazine, $H_2[pz(Pr)_8]$, is relatively hard to oxidize, having a first oxidation potential of +0.68 V.[33] However, the freebase porphyrazine **7** exhibits two reversible ring oxidations at $E_{1/2} = -0.13$ and +0.43 V (vs Fc^+/Fc) (Figure 5). Thus, replacement of two propyl chains by two dimethyl-

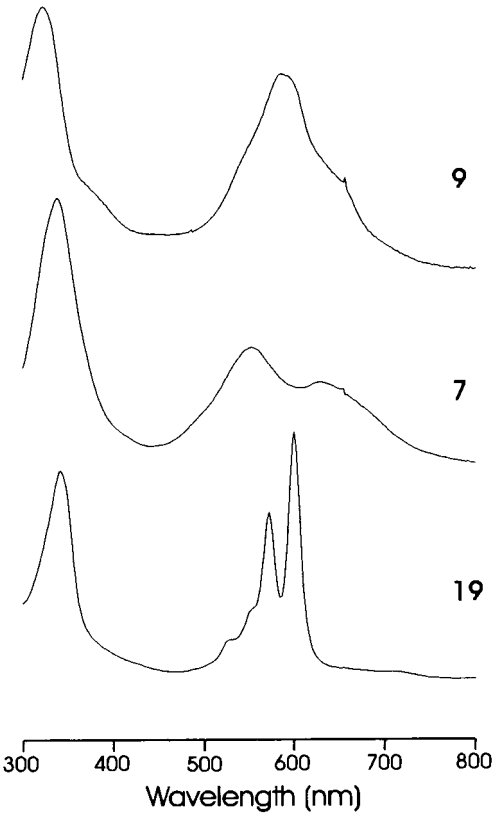

Figure 4. Representative UV−visible spectra for (a) centrally Cu(II)-metalated, (b) metal-free, and (c) peripherally $PtCl_2$-coordinated porphyrazines.

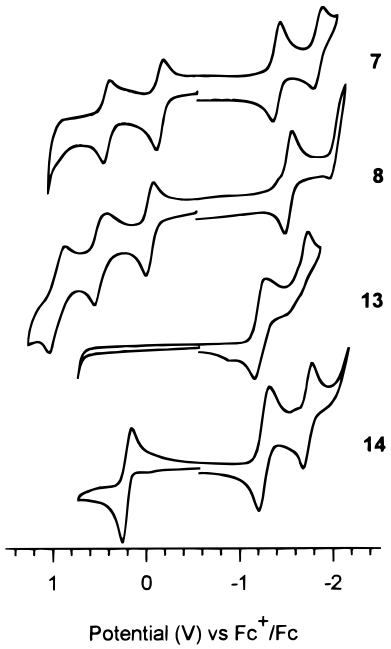

Figure 5. Cyclic voltammograms of (a) 2H porphyrazine **7**, (b) Ni(II) porphyrazine **8**, (c) PdMNT-capped porphyrazine **13**, and (d) PdBDT-capped porphyrazine **14** taken in dichloromethane.

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Table 5. Electrochemical Data in Dichloromethane (Volts vs Fc^+/Fc)[a]

	$E_{1/2}$ (ΔE_p, mV)					
cpd	Ni^{III}/Ni^{II}	Pz^{2+}/Pz^+	Pz^+/Pz	M'^{III}/M'^{IIb}	Pz/Pz^{-1}	Pz^{-1}/Pz^{-2}
7		+0.43 (66)	−0.13 (70)		−1.39 (76)	−1.84 (94)
8	+0.90 (120)	+0.47 (120)	−0.06 (76)		−1.55 (90)	
11			+0.92 (90)		−1.26 (E_{pc})	−1.63 (E_{pc})
13			+0.94 (E_{pa})		−1.22 (120)	−1.73 (E_{pc})
14			+1.03 (E_{pa})	+0.22 (90)	−1.27 (110)	−1.73 (90)
15			+1.03 (E_{pa})	+0.19 (98)	−1.22 (100)	−1.70 (E_{pc})
21			+0.91 (E_{pa})	+0.20 (89)	−1.20 (86)	−1.69 (E_{pc})
22			+0.81 (E_{pa})	+0.19 (82)	−1.18 (86)	−1.65 (E_{pc})

[a] Measured in solutions ca. 10^{-3} M in compound and 0.1 M in $[N(C_4H_9\text{-}n)_4]PF_6$ at a Pt disk working electrode with a scan rate of 110 mV s^{-1}. [b] M′ = Pd for **14** and **15**, M′ = Pt for **21** and **22**.

amino moieties shifts $E°$ by approximately 0.8 V. In fact, the first oxidation of **7** occurs only 140 mV to higher potential than what was seen for octakis(dimethylamino)tetraazaporphyrin (first oxidation potential = −0.27 V), the most easily oxidized porphyrazine prepared to date.[6] The MnO_2-mediated oxidation of **7** that leads to pyrrole bond cleavage and formation of the *seco*-porphyrazine was the subject of a recent report.[34] In addition to the two oxidations, **7** displays two reversible ring reductions at −1.39 and −1.84 V (vs Fc^+/Fc) (Figure 5). Central metalation with Ni(II) in **8** results in the loss of one reduction wave in the cyclic voltammogram and the gain of a non-Nernstian macrocycle oxidation at +0.90 V. These data are collected in Table 5.

The cyclic voltammograms of the metal-dithiolene capped porphyrazines reveal a reversible oxidation couple arising from the peripheral $[N_2-M-S_2]$ functionality, formally written as M(II/III) (M = Pt, Pd) (Figure 5). These oxidations occur at approximately +0.2 V (vs Fc^+/Fc) for the Pd(dmid), Pd(bdt), Pt(tdt), and Pt(dmit) capped porphyrazines, compounds **14**, **15**, **21**, and **22** respectively (Table 5). However, in all cases, chemical oxidation resulted in decomposition to form oxidized ligand, as confirmed by electron paramagnetic resonance spectroscopy, and we were unable to isolate the one-electron oxidized species. It is interesting to note that within the electrochemical window available in dichloromethane, this couple is not observed for the mnt^{2-}-capped compound **13** (Figure 5). The electron-withdrawing character of the maleonitrile unit likely destabilizes the peripherally oxidized state of **13**.

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Conclusions

We have synthesized tetraazaporphyrin substituted at the periphery with a single bidentate dimethylamino chelating group and demonstrated that this new ligand will coordinate $PdCl_2$ and $PtCl_2$. The chlorine ligands were substituted for dithiolato ligands and the first stable heteroleptic bis(amine)dithiolene palladium(II) complex was synthesized and structurally characterized. As a step toward the synthesis of metal-linked multiporphyrazine arrays, we have assembled the bis(palladium)-(btt)-bridged porphyrazine dimers (**16** and **17**). Although the heteroleptic palladium(II) complexes with electron rich dithiolene ligands were unstable toward disproportionation, the analagous platinum(II) complexes exhibited greatly enhanced stability. This "hook and eye" technique involving reaction of stable N_2MCl_2 species with dithiolene ligands, possibly using the diamino rather than bis(dimethylamino) chelates, will allow us to combine porphyrazine thiolates and assemble even higher-order metal-linked porphyrinic arrays.

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Supporting Information Available: X-ray structural details for **13** (23 pages). Ordering information is given on any current masthead page.

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