larization) and should allow us to investigate the idea of "surface islanding" of the adsorbed molybdates.

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Syntheses and Spectroscopic Characterization of $(T(p\text{-}Me_2N)F_4PP)H_2$ and $(T(p\text{-}Me_2N)F_4PP)M$ Where $T(p\text{-}Me_2N)F_4PP$ Is the Dianion of *meso*-Tetrakis(*o*,*o*,*m*,*m*-tetrafluoro-*p*-(dimethylamino)phenyl)porphyrin and M = Co(II), Cu(II), or Ni(II). Structures of $(T(p\text{-}Me_2N)F_4PP)Co$ and (*meso*-Tetrakis(pentafluorophenyl)porphinato)cobalt(II), $(TF_5PP)Co$

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Abstract: The reaction of cobalt acetate with $(TF_5PP)H_2$ (where TF_5PP = the dianion of *meso*-tetrakis(pentafluorophenyl)porphyrin) leads to the formation of different metalloporphyrin products depending on solvent. In acetonitrile, $(TF_5PP)Co$ is the expected and obtained product of metalation. In contrast, the reaction between $(TF_5PP)H_2$ and cobalt acetate in dimethylformamide leads to $(T(p\text{-}Me_2N)F_4PP)Co$ where $T(p\text{-}Me_2N)F_4PP$ = the dianion of *meso*-tetrakis(*o*,*o*,*m*,*m*-tetrafluoro-*p*-(dimethylamino)phenyl)porphyrin. The formation of a dimethylamino-substituted complex in DMF is not unique to cobalt derivatives, and $(T(p\text{-}Me_2N)F_4PP)H_2$, $(T(p\text{-}Me_2N)F_4PP)Cu$, or $(T(p\text{-}Me_2N)F_4PP)Ni$ were synthesized from $(TF_5PP)H_2$ in almost 100% yield. Each $T(p\text{-}Me_2N)F_4PP$ complex was isolated and characterized by ^{1}H NMR, ^{19}F NMR, and UV–visible spectroscopy as well as by mass spectrometry. These compounds provide the first examples for substituted tetraphenylporphyrins where the four phenyl rings contain both electron-withdrawing and electron-donating substituents. The pentafluoro-substituted Co(II) derivative, $(TF_5PP)Co$, was also synthesized and spectroscopically characterized. In addition, both Co(II) porphyrins were analyzed by X-ray single-crystal diffraction. $(TF_5PP)Co$ crystallizes in the monoclinic space group $I2/c$, with $a = 29.200$ (13) Å, $b = 6.552$ (2) Å, $c = 26.381$ (10) Å, $\beta = 104.13$ (3)°, and $Z = 4$ while $(T(p\text{-}Me_2N)F_4PP)Co$ is found to crystallize in the triclinic space group $P\bar{1}$ with $a = 13.638$ (9) Å, $b = 14.645$ (8) Å, $c = 16.677$ (9) Å, $\alpha = 79.98$ (4)°, $\beta = 77.89$ (5)°, $\gamma = 65.92$ (4)°, and $Z = 2$.

Introduction

The synthesis of 5,10,15,20-tetrakis(pentafluorophenyl)porphine, $(TF_5PP)H_2$, was first reported in 1969 and was followed by a number of studies on the synthesis, characterization, and chemical reactivity of the free base complex[1–6] or its metalated derivatives.[1,7–12] Recently, however, Gouterman et al.[13] demonstrated that the refluxing of $(TF_5PP)H_2$ and $AgNO_3$ in acetic acid does not result in formation of the expected $(TF_5PP)Ag$ product but rather gives a porpholactone derivative. Cu and Ni porpholactone (or porphodilactone) derivatives were also synthesized by the same method in acetic acid.[13]

N,*N*-Dimethylformamide (DMF) is a common solvent for metalation of a free base porphyrin,[14] and the syntheses of $(TF_5PP)Zn$, $(TF_5PP)Cu$, and $(TF_5PP)Pd$ were reported to occur without complication in this solvent.[1,9] However, as will be demonstrated in this paper, the metalation of $(TF_5PP)H_2$ in DMF is neither straightforward nor does it give the expected porphyrin products which have been reported and spectroscopically characterized over the last 20 years. Complexes of $(TF_5PP)M$ can

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be obtained by metalation of $(TF_5PP)H_2$ in acetonitrile, chloroform, or toluene but attempts to carry out the same reaction in DMF result only in formation of *meso*-tetrakis(*o*,*o*,*m*,*m*-tetrafluoro-*p*-(dimethylamino)phenyl)porphinato complexes of the type $(T(p\text{-}Me_2N)F_4PP)M$. A similar reaction also occurs by refluxing free base $(TF_5PP)H_2$ in DMF and gives only $(T(p\text{-}Me_2N)F_4PP)H_2$ as a final porphyrin product.

In this present paper, $(T(p\text{-}Me_2N)F_4PP)H_2$ and $(T(p\text{-}Me_2N)F_4PP)M$ where M = Co(II), Cu(II), Ni(II) were synthesized and characterized by ^1H NMR, ^{19}F NMR, and UV-visible spectroscopy as well as by mass spectrometry. $(TF_5PP)Co$ was also synthesized and spectroscopically characterized. X-ray structures of $(T(p\text{-}Me_2N)F_4PP)Co$ and $(TF_5PP)Co$ are both presented.

Experimental Section

Chemicals and Reagents. Deuterated chloroform ($CDCl_3$) was purchased from Aldrich Chemical Co. CH_2Cl_2 was obtained as spectroscopic grade from Fisher Scientific Co. and twice distilled over calcium hydride (CaH_2). Solvents used for synthesis or NMR measurements were used as received, while those for UV-visible measurements were distilled prior to use. $(TF_5PP)H_2$ was purchased from Aldrich. Its identity and purity was confirmed by mass spectrometry as well as by ^1H and ^{19}F NMR spectroscopy.

Physical Measurements. ^1H NMR spectra were recorded on a QE-300 FT NMR spectrometer using $CDCl_3$ as solvent. Chemical shifts were referenced against tetramethylsilane (TMS). ^{19}F NMR spectra were obtained with a JEOL FX 90Q FT NMR spectrometer which was coupled to a Wavetek Rockland Model 5610 frequency synthesizer by using Freon ($CFCl_3$) as an internal standard. Samples for ^{19}F NMR were measured in $CDCl_3$. UV-visible spectra were recorded with an IBM 9430 spectrophotometer.

Mass spectra were obtained from a high-resolution hybrid tandem VG Analytical Model 70-SEQ (EEQQ geometry) mass spectrometer. A standard fast atom bombardment (FAB) source was used, and *m*-nitrobenzyl alcohol (NBA) was the liquid matrix.

Elemental analysis was carried out by Schwarzkopf Microanalytical Laboratory, Woodside, NY.

Synthesis of $(TF_5PP)Co$. $(TF_5PP)Co$ was synthesized by refluxing 0.4 mmol of $(TF_5PP)H_2$ and 4.0 mmol of $Co(C_2H_3O_2)_2{\cdot}4H_2O$ (Allied Chemical Co.) in 400 mL of CH_3CN (Mallinckrodt, Inc.—ChromAR·HPLC) for 12 h. The solution was filtered, and the solvent was evaporated. The dried product was then chromatographed on a neutral alumina column (Aldrich Chemical Co.—150 mesh) by using benzene (J. T. Baker Inc.—"Baker Analyzed") as the eluting solvent to remove unreacted $Co(C_2H_3O_2)_2{\cdot}4H_2O$. The collected solution was then passed through a neutral alumina column by using a 9:1 hexane/benzene mixture as the eluting solvent. The first of the three bands which eluted was brown and was identified as unreacted $(TF_5PP)H_2$. The second was red-purple in color and was the desired product, $(TF_5PP)Co$. The third band was blue-green and was due to a chlorin impurity.

The second band, which corresponded to $(TF_5PP)Co$, was collected and twice chromatographed by using a column of neutral alumina with hexane as the eluting solvent. The final product was slowly recrystallized from a 4:1 mixture of benzene and cyclohexane and gave a yield of about 60%. Needle-like purple crystals formed and were identified as $(TF_5PP)Co$. The same product could also be obtained by metalation of $(TF_5PP)H_2$ in toluene or chloroform: UV-visible data [λ, nm ($\epsilon \times 10^{-4}$, $M^{-1}\,cm^{-1}$)] CH_2Cl_2 403 (21.2), 524 (1.0), 552 (0.8); mass spectral data calcd MW, 1031.0; *m/e* of parent peak 1031. Anal. Calcd for $C_{44}H_8N_4F_{20}Co{\cdot}{}^3/_2C_6H_6$: C, 55.42; H, 1.49; N, 4.88; F, 33.08; Co, 5.13; mol wt 1149. Found: C, 55.07; H, 1.50; N, 4.88; F, 32.42; Co, 5.29.

Synthesis of $(T(p\text{-}Me_2N)F_4PP)Co$. $(T(p\text{-}Me_2N)F_4PP)Co$ was prepared by refluxing 0.4 mmol of $(TF_5PP)H_2$ and 4.0 mmol of $Co(C_2H_3O_2)_2{\cdot}4H_2O$ in 500 mL of DMF for 12 h. The dried product was chromatographed on a column of neutral alumina with benzene as the eluting solvent. Unreacted $Co(C_2H_3O_2)_2{\cdot}4H_2O$ is insoluble in benzene and remained at the top of the column. The eluate was collected and chromatographed twice on a neutral alumina column by using CH_2Cl_2 as the mobile phase. The compound isolated from the eluate was slowly recrystallized from a 1:9 mixture of CH_2Cl_2 and benzene. Purple needle-like crystals were identified as $(T(p\text{-}Me_2N)F_4PP)Co$. The yield was nearly 100%. UV-visible data [λ, nm ($\epsilon \times 10^{-4}$, $M^{-1}\,cm^{-1}$)] CH_2Cl_2 410 (25.7), 526 (1.7), 553 (0.9); mass spectral data calcd MW 1131.2; *m/e* of parent peak 1131. Anal. Calcd for $C_{52}H_{32}N_8F_{16}Co$: C, 55.17; H, 2.83; N, 9.90; F, 26.88; Co, 5.22; mol wt 1132. Found: C, 54.33; H, 3.20; N, 9.54; F, 25.55; Co, 5.24.

Synthesis of $(T(p\text{-}Me_2N)F_4PP)M$ where M = Cu(II) or Ni(II). $(T(p\text{-}Me_2N)F_4PP)Cu$ and $(T(p\text{-}Me_2N)F_4PP)Ni$ were prepared by refluxing 0.4 mmol of $(TF_5PP)H_2$ with 4.0 mmol of $Cu(C_2H_3O_2)_2{\cdot}H_2O$ (Fisher Scientific Co.—ACS) or $Ni(C_2H_3O_2)_2{\cdot}4H_2O$ (Fisher Scientific Co.—ACS) in DMF for 12 h. The dried product was filtered with benzene to remove unreacted Cu or Ni acetate and then chromatographed on a column of neutral alumina with CH_2Cl_2 as the eluting solvent. The orange or brown band was collected, and the compounds obtained after solvent evaporation were identified as either $(T(p\text{-}Me_2N)F_4PP)Cu$ or $(T(p\text{-}Me_2N)F_4PP)Ni$. UV-visible data [λ, nm ($\epsilon \times 10^{-4}$, $M^{-1}\,cm^{-1}$)] $(T(p\text{-}Me_2N)F_4PP)Cu$, CH_2Cl_2 414 (25.4), 537 (1.8), 570 (0.4); $(T(p\text{-}Me_2N)F_4PP)Ni$, CH_2Cl_2 412 (18.3), 526 (1.6), 557 (0.8); mass spectral data $(T(p\text{-}Me_2N)F_4PP)Cu$; calcd MW 1135.2; *m/e* of parent peak 1136; $(T(p\text{-}Me_2N)F_4PP)Ni$, calcd MW 1130.2; *m/e* of parent peak 1131.

Table I. Data Collection and Processing Parameters

	$(T(p\text{-}Me_2N)F_4PP)Co$	$(TF_5PP)Co$
space group	$P\bar{1}$	$I2/c$
cell const		
a, Å	13.638 (9)	29.200 (13)
b, Å	14.645 (8)	6.552 (2)
c, Å	16.677 (9)	26.381 (10)
α, deg	79.98 (4)	
β, deg	77.89 (5)	104.13 (3)
γ, deg	65.92 (4)	
V, $Å^3$	2959	4894
mol formula	$C_{52}H_{32}N_8F_{16}Co{\cdot}2C_6H_6$	$C_{44}H_8N_4F_{20}Co{\cdot}2C_6H_6$
fw	1288.09	1187.3
Z	2	4
ρ (calc), g/cm^3	1.45	1.61
μ, cm^{-1}	3.83	4.66
λ (Mo Kα), Å	0.71073	0.71073
$R\ (F_o)$	0.059	0.048
$R_w\ (F_o)$	0.042	0.032

Synthesis of $(T(p\text{-}Me_2N)F_4PP)H_2$. $(T(p\text{-}Me_2N)F_4PP)H_2$ was prepared by refluxing 0.4 mmol of $(TF_5PP)H_2$ in DMF for 12 h. The dried product was chromatographed on a column of neutral alumina by using CH_2Cl_2 as the eluting solvent. The collected eluate was twice chromatographed on a neutral alumina column by using a 1:1 mixture of benzene/hexane as the eluting solvent. The brown band was collected, and the compound obtained after solvent evaporation was identified as $(T(p\text{-}Me_2N)F_4PP)H_2$: UV-visible data [λ, nm ($\epsilon \times 10^{-4}$, $M^{-1}\,cm^{-1}$)] CH_2Cl_2 419 (28.3), 510 (2.1), 544 (0.5), 586 (0.7), 641 (0.07); mass spectral data calcd MW 1074.3; *m/e* of parent peak 1076.

X-ray Crystallography. Single-crystal X-ray studies of $(T(p\text{-}Me_2N)F_4PP)Co$ and $(TF_5PP)Co$ were performed at the University of Houston X-ray Crystallographic Center. Samples of both compounds were coated with a thin layer of epoxy to retard solvent loss and mounted in a random orientation on a Nicolet R3m/V automatic diffractometer. The radiation used was Mo Kα monochromatized by a highly ordered graphite crystal. Two standard reflections were measured after every 2 h or after every 100 data points collected, and these showed no significant variation. In reducing the data, Lorentz and polarization corrections were applied, but no corrections for absorption were made due to the small absorption coefficients. Final cell constants as well as other information pertinent to data collection and refinement are listed in Table I. All calculations were made by using Nicolet's SHELXTL PLUS (1988) series of crystallographic programs. All shift-esd ratios were less than 0.5 (except those involving disordered solvent), and convergence was reached at the agreement factors listed in Table I. No unusually high correlations were noted between any of the variables in the last cycle of full-matrix least-squares refinement, and in both cases the final difference density map showed a maximum peak of less than 0.4 e/$Å^3$.

The structure of the dimethylamino-substituted derivative was solved by the Patterson method, which revealed the asymmetric unit to consist of two independent half-molecules situated on inversion centers. Hydrogens were entered in ideal calculated positions and constrained to riding motion, with a single nonvariable isotropic temperature factor for each of the porphyrin and methyl hydrogen types. Disordered benzene molecules of solvation were found near both of the Co positions and were refined as rigid bodies with single variable isotropic temperature factors. The individual occupancies were determined by varying them temporarily while fixing the temperature factors. The population factors were found to be 55%:45% for C27:C27A and 65%:35% for C59:C59A and were held fixed in the final cycles of refinement.

The Laue symmetry of the pentafluorophenylporphyrin compound was found to be 2/*m*, and from the systematic absences noted for both the I- and C-centered cells the space group was shown to be either *Ic* or *I*2/*c*. The conventional end-centered cell was not used in this case since that cell has a β angle much further from 90°. Since the molecule is capable of possessing internal symmetry, space group *I*2/*c* was assumed from the outset. The structure was solved by use of the SHELXTL direct methods program, which revealed the asymmetric unit to consist of one-half

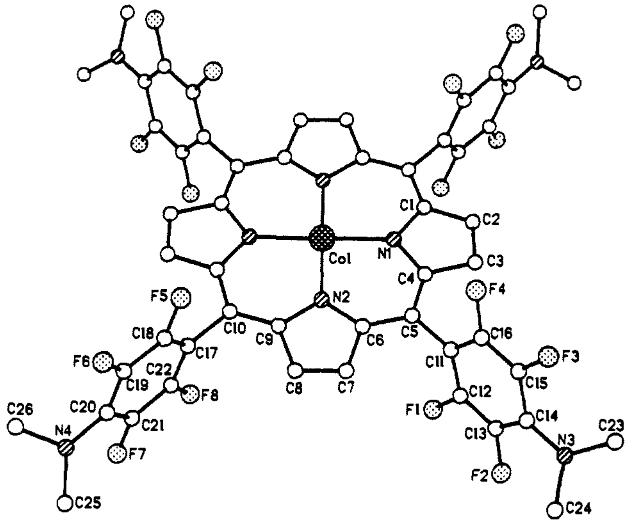

Figure 1. View of (T(p-Me_2N)F_4PP)Co, with hydrogens omitted for clarity. The benzene solvent (not shown) is numbered C27–C32. To obtain atom labels for the Co2 molecule, add 8 to F, 4 to N, and 32 to C numbers shown.

Table II. Average Bond Lengths (Å)[a]

atom 1	atom 2	(T(p-Me_2N)F_4PP)Co	(TF_5PP)Co
Co	N(por)	1.971 (6)	1.976 (5)
C(ph)	F	1.346 (15)	1.333 (15)
C(por)	C(ph)	1.491 (13)	1.495 (9)
C(ph)	N(p-am)	1.38 (2)	
N(p-am)	C(me)	1.39 (2)	

[a] Por = porphyrin; ph = phenyl; me = methyl; p-am = p-N,N-dimethylamine.

Table III. Torsion Angles (deg)

	(T(p-Me_2N)F_4PP)Co[a]		
N2–Co1–N1–C1	179.1	N6–Co2–N5–C33	178.2
N1–Co1–N2–C9	−179.2	N5–Co2–N6–C41	177.9
C4–C5–C11–C16	74.8	C36–C37–C43–C44	−86.1
C9–C10–C17–C22	−87.2	C41–C42–C49–C50	91.5
C13–C14–N3–C24	−44.0	C45–C46–N7–C56	−44.7
C19–C20–N4–C26	57.6	C51–C52–N8–C58	29.9
	(TF_5PP)Co		
N1–Co–N2–C9	178.0	C4–C5–C11–C12	75.5
N2–Co–N1–C1	−179.8	C9–C10–C17–C22	−75.7

[a] Individual (not average) values.

molecule situated about an inversion center. All hydrogens were entered in ideal calculated positions and constrained to riding motion, with a single variable isotropic temperature factor. Two benzene molecules of solvation were found, each disordered about an inversion center. Both orientations at each of the two sites were found to be present in 50% occupancy. Ideal rigid bodies of one-half benzene ring constrained to lie a fixed distance from the inversion center were used as models, with a single variable isotropic temperature factor for each site.

Results and Discussion

Structural Characterization of (T(p-Me_2N)F_4PP)Co and (TF_5PP)Co. The two molecules are shown in Figure 1 and 2. Tables II and III show selected bond lengths and torsion angles. All intramolecular bond lengths and angles as well as other structural data are given as supplementary material. As can be seen from these tables, the basic molecular geometries are quite similar for the two compounds. In both compounds the molecules are positioned on crystallographic inversion centers which implies that the metal atoms are exactly in the center of the two planes which are defined by the four nitrogen atoms and the 24 atom porphyrin core.

The coordination about the cobalt atom is square planar (see Figures 1 and 2). The average Co–N distance is 1.971 (6) Å for (T(p-Me_2N)F_4PP)Co and 1.976 (5) Å for (TF_5PP)Co. These values are typical for a cobalt(II) porphyrin where the porphyrin core is nearly planar and slightly longer than the value of 1.949 (5) Å found in (TPP)Co, where the core is quite ruffled.[15] The maximum deviation from planarity of any core atom in the fluorinated compounds is only 0.05 Å, essentially flat. The phenyl rings are twisted about 75° with respect to the (TF_5PP)Co core, which is similar to the non-fluorinated counterparts. However, in both independent molecules of the dimethylamino-substituted derivative, some of the phenyl rings are twisted by 86 to 89°. Since there is no obvious electronic or steric force involved, this phenomenon is attributed simply to crystallographic packing forces between neighboring molecules.

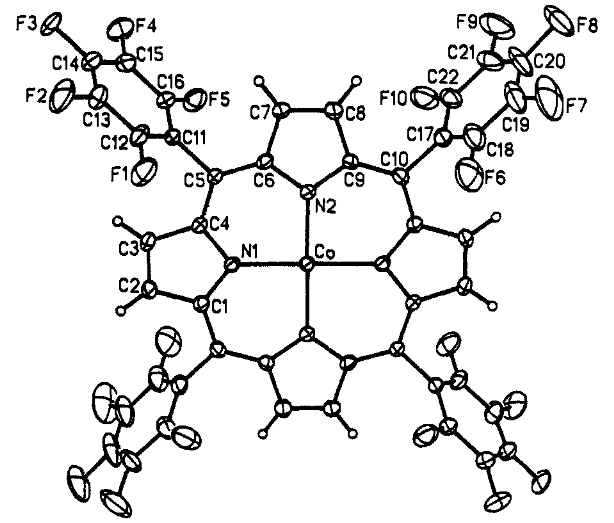

Figure 2. View of (TF_5PP)Co showing the atom-numbering scheme. The thermal ellipsoids are 20% equiprobability envelopes, with hydrogens as spheres of arbitrary diameter.

Each porphyrin ring is sandwiched by two benzene molecules of solvation, one above and one below the plane (see supplementary material). In the p-Me_2N derivative, the individual benzenes are localized on a given porphyrin, whereas in the TF_5PP derivative the benzenes are each shared, being exactly midway between two porphyrins. There are additional channels of lone solvent molecules running through the cell along the b axis in the latter compound. The obvious conclusion from these observations is that there is some weak π-bonding between the metalloporphyrin and the aromatic solvent, as has been frequently observed.[16] In general, separations of less than 3.3 Å are thought to indicate definite π interaction. In (TF_5PP)Co, the benzene ring centroid is 3.18 Å from the porphyrin mean plane, and the dihedral angle between the two planes is 6°. In (T(p-Me_2N)F_4PP)Co, the average ring centroid is 3.25 Å from the core, and the average dihedral angle is 9°. Thus, the substitution at the para positions of the phenyl substituents does not seem to have a major effect on the π-acceptor character of the metalloporphyrin. The stacking of the molecules along the b axis in (TF_5PP)Co suggests that some long-range charge transfer might be possible in this compound. However, this has not been investigated.

Synthesis and Reaction Mechanism. The reactions between (TF_5PP)H_2 and Co(II), Ni(II), or Cu(II) acetate in DMF or CH_3CN were monitored by UV–visible spectroscopy. The UV–visible spectrum of (TF_5PP)H_2 and the resulting Co acetate metalation products in each of the two solvents are shown in Figure 3. (TF_5PP)H_2 in DMF has a Soret band at 408 nm and Q bands located at 504, 532, 579, and 654 nm. In CH_3CN, these bands are located at 407, 503, 535, 578, and 652 nm. The cobalt metalation product formed in DMF (solid line Figure 3a) has a Soret band at 413 nm and two visible or Q bands at 527 and 549 nm. This spectrum differs only slightly from that of the product obtained in CH_3CN which has a Soret band at 404 nm and Q

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Table IV. ^{1}H and ^{19}F NMR Data in CDCl$_3$[a]

compound	^{1}H NMR -N(CH$_3$)$_2$	^{1}H NMR β-pyrrole	^{1}H NMR core	^{19}F NMR *o*-F	^{19}F NMR *m*-F	^{19}F NMR *p*-F
(TF$_5$PP)H$_2$		8.91 (s)	-2.92 (s)	-137.0 (d)	-161.8 (t)	-151.7 (t)
(T(*p*-Me$_2$N)F$_4$PP)H$_2$	3.27 (s)	8.93 (s)	-2.88 (s)	-140.3 (s)	-152.5 (s)	
(TF$_5$PP)Co		15.0[b]		-133.4 (s)	-160.4 (s)	-150.6 (s)
(T(*p*-Me$_2$N)F$_4$PP)Co	4.17 (s)	15.2[b]		-136.6 (s)	-150.8 (s)	
(T(*p*-Me$_2$N)F$_4$PP)Ni	3.27 (s)	8.79 (s)		-140.4 (s)	-152.3 (s)	
(T(*p*-Me$_2$N)F$_4$PP)Cu	3.18 (s)	*c*		-141.5[b]	-153.0 (s)	

[a] In ppm; s = singlet; d = doublet; t = triplet. [b] Broad. [c] Not visible (see ref 24).

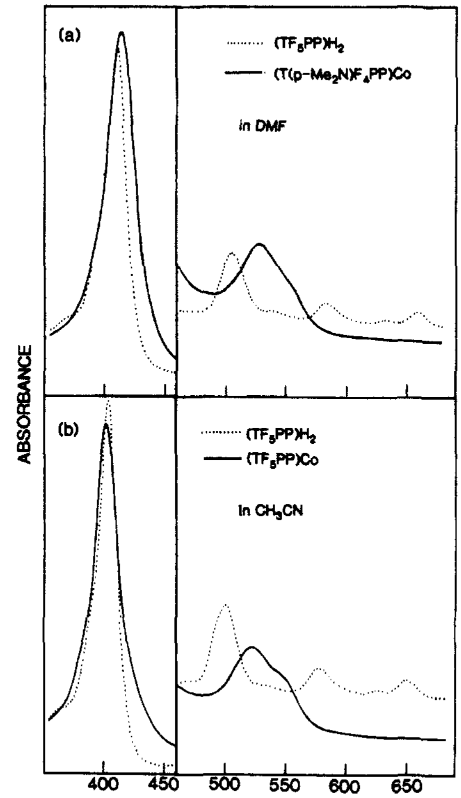
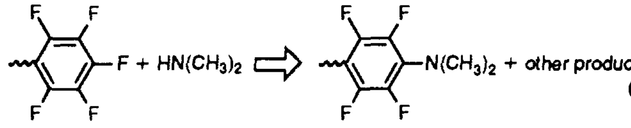


Figure 3. UV-visible spectra before and after metalation of (TF$_5$PP)H$_2$ by Co(II) in (a) DMF and (b) CH$_3$CN.

bands at 524 and 550 nm (solid line in Figure 3b). The Q(0,0) bands of both (TF$_5$PP)Co and (T(*p*-Me$_2$N)F$_4$PP)Co are more intense than the corresponding band of (TPP)Co under similar solution conditions, which suggests a stronger perturbation by the central metal in the two fluorinated porphyrins.[17]

The UV-visible spectra provide little information as to the formation of different porphyrin metalation products, but this is not the case for the mass spectral data which are quite definitive. Mass spectra of the two cobalt products are consistent with calculated molecular weights of 1131.2 for (T(*p*-Me$_2$N)F$_4$PP)Co and 1031.0 for (TF$_5$PP)Co. They are also consistent with the elemental mass analysis data (see Experimental Section) as well as with the two X-ray structures discussed earlier.

DMF is known to decompose during reflux and results in the formation of dimethylamine under conditions similar to those reported in this present paper.[18] The generated amine may complex to a porphyrin metal center as was demonstrated for the case of (P)RhCl which was converted to (P)Rh[N(CH$_2$)$_2$]$_2$$^+$ in DMF during reflux.[19] Alternatively, the amine may also replace a fluorine atom on one or more phenyl rings of the TF$_5$PP complex via the activated aromatic nucleophilic substitution (S$_N$Ar) reaction shown in eq 1.



(1)

Reaction 1 is known to occur under mild conditions when a phenyl ring bears both strongly electron-withdrawing substituents and good leaving groups[20] such as fluorine atoms. Although resonance structures for the S$_N$Ar transition state would indicate that the nucleophile can attack at either the ortho or para position (but not the meta position) of the pentafluoro phenyl ring,[21] the high (almost 100%) yield of (T(*p*-Me$_2$N)F$_4$PP)Co suggests that the substitution in this case occurs exclusively at the para position, presumably due to steric factors.

A similar reaction will also occur between pentafluoroporphyrin complexes and gaseous HN(CH$_3$)$_2$ in toluene but leads to a mixture of several products. For example, the refluxing of (TF$_5$PP)H$_2$ and HN(CH$_3$)$_2$ for 12 h gives a product which has three bands on an alumina column with a 3:1 mixture of hexane and benzene as the eluting solvent. Mass spectral data of the pure isolated products have parent peaks at *m/e* values of 976, 1000, and 1025. These values correspond to a pentafluoro free base chlorin (*m/e* = 976) and a free base porphyrin with one (*m/e* = 1000) or two (*m/e* = 1025) of the four phenyl rings substituted by N(CH$_3$)$_2$. UV-visible spectra confirm the chlorin or porphyrin nature of each isolated product. The fully substituted (T(*p*-Me$_2$N)F$_4$PP)H$_2$ species has a theoretical *m/e* value of 1074.3 and is not observed. Presumably, this is due to the different experimental conditions for generation of HN(CH$_3$)$_2$.

Spectroscopic Characterization of (T(*p*-Me$_2$N)F$_4$PP)Co and (TF$_5$PP)Co. A summary of ^{1}H and ^{19}F NMR data for (T(*p*-Me$_2$N)F$_4$PP)Co and (TF$_5$PP)Co is given in Table IV. The ^{1}H NMR spectrum of (T(*p*-Me$_2$N)F$_4$PP)Co in CDCl$_3$ has three distinct resonances. The resonances due to the β-pyrrole protons of the porphyrin macrocycle are observed as a broad peak at 15.2 ppm and are downfield shifted due to the presence of the paramagnetic cobalt(II) center. There is also a sharp peak at 4.17 ppm which arises from the protons of the dimethylamino groups. Integration of the two signals at 15.2 and 4.17 ppm gives a 1:3 ratio which is consistent with the presence of eight β-pyrrole hydrogens and 24 dimethylamino hydrogens per porphyrin molecule. An intense peak at 7.16 ppm is also observed and is attributed to benzene solvent molecules. Benzene is also present in the solid state of (T(*p*-Me$_2$N)F$_4$PP)Co as illustrated by the X-ray structure (see supplementary material).

The proton NMR spectrum for (TF$_5$PP)Co is characterized by two major resonances. There is a broad peak at 15.0 ppm due to the β-pyrrole hydrogens of the macrocycle and an intense peak at 7.16 ppm which arises from the benzene molecules of solvation. The absence of a resonance at higher fields is in agreement with the absence of a dimethylamino group on the phenyl rings and is consistent with the results obtained from X-ray crystallography.

^{19}Fluorine NMR spectra of the two cobalt complexes and of (TF$_5$PP)H$_2$ in deuterated chloroform are shown in Figure 4. The

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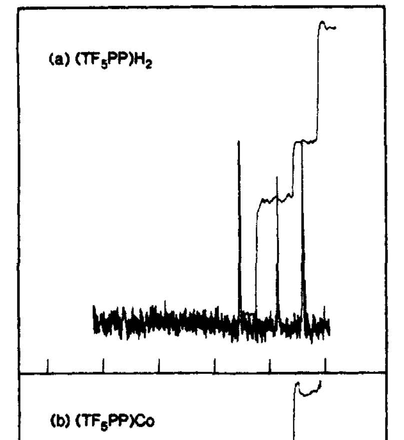

Figure 4. ^{19}F NMR spectra of (a) (TF$_5$PP)H$_2$, (b) (TF$_5$PP)Co, and (c) (T(*p*-Me$_2$N)F$_4$PP)Co in CDCl$_3$.

free base complex (TF$_5$PP)H$_2$ (Figure 4a) has three fluorine resonances (see Table IV). The resonances for the meta fluorine groups are the most upfield shifted and appear as a triplet at −161.8 ppm. A triplet signal is also observed at −151.7 ppm and is due to the fluorine atoms at the para position of each phenyl group. The ortho fluorine atoms are the most downfield shifted and appear as a doublet at −137.0 ppm. As expected, integration of these signals gives a ratio of 2:1:2 for fluorines at the ortho, para, and meta positions of the phenyl ring on (TF$_5$PP)H$_2$. The fluorine resonances of (TF$_5$PP)H$_2$ are comparable to values given in the literature for other pentafluorobenzene derivatives.[22,23] In contrast, the ^{19}F NMR spectra of free base (T(*p*-Me$_2$N)F$_4$PP)H$_2$ has only two fluorine resonances. The resonance corresponding to the ortho fluorines occurs at −140.3 ppm while that of the meta fluorines occurs at −152.5 ppm. ^{1}H NMR and ^{19}F NMR spectral data of (T(*p*-Me$_2$N)F$_4$PP)H$_2$ and (TF$_5$PP)H$_2$ are summarized in Table IV. UV–visible data for (T(*p*-Me$_2$N)F$_4$PP)H$_2$ are given in the Experimental Section.

The ^{19}F NMR spectra of (T(*p*-Me$_2$N)F$_4$PP)Co and (TF$_5$PP)Co have somewhat broader peaks compared to those for free base (TF$_5$PP)H$_2$ or (T(*p*-Me$_2$N)F$_4$PP)H$_2$. This is due to the presence of the paramagnetic cobalt(II) center. The spectrum of (TF$_5$PP)Co (Figure 4b) is similar to the one for (TF$_5$PP)H$_2$ and shows fluorine resonances at −133.4, −150.6, and −160.4 ppm. These are assigned to fluorine atoms at the ortho, para, and meta positions of the four phenyl rings, respectively. In contrast, the ^{19}F NMR spectrum of (T(*p*-Me$_2$N)F$_4$PP)Co has only two distinct resonances, at −136.6 and −150.8 ppm, with an integration ratio of 1:1 (see Figure 4c). These two peaks are attributed to fluorines at each ortho and meta position of the porphyrin's four phenyl groups. The peak for the meta fluorine atoms of (T(*p*-Me$_2$N)F$_4$PP)Co appear at lower fields compared to those of (TF$_5$PP)H$_2$ or (TF$_5$PP)Co and this is due to the proximity of these fluorine atoms to an electron donor amino group.

Spectroscopic Characterization of (T(*p*-Me$_2$N)F$_4$PP)Ni and (T(*p*-Me$_2$N)F$_4$PP)Cu. Mass spectra of the products isolated after refluxing Ni or Cu acetate and (TF$_5$PP)H$_2$ in DMF show parent peaks consistent with the calculated molecular weights for (T(*p*-Me$_2$N)F$_4$PP)Ni or (T(*p*-Me$_2$N)F$_4$PP)Cu, i.e., 1130.2 amu for M = Ni(II) and 1135.2 amu for M = Cu(II).

^{1}H and ^{19}F NMR spectral data for (T(*p*-Me$_2$N)F$_4$PP)Ni and (T(*p*-Me$_2$N)F$_4$PP)Cu are summarized in Table IV and are similar to data reported above for (T(*p*-Me$_2$N)F$_4$PP)Co. The ^{19}F NMR spectra shows two resonances of equal intensity at −140.4 and −152.3 ppm for (T(*p*-Me$_2$N)F$_4$PP)Ni and at −141.5 and −153.0 ppm for (T(*p*-Me$_2$N)F$_4$PP)Cu. These are due to the fluorines at the ortho and meta positions of the four phenyl rings. The proton NMR spectrum of (T(*p*-Me$_2$N)F$_4$PP)Ni shows two resonances at 3.27 and 8.79 ppm which have an integration ratio of 3:1. These two peaks are attributed to the β-pyrrole hydrogens and the dimethylamino group hydrogens attached to the phenyl substituents. The β-pyrrole hydrogens of (T(*p*-Me$_2$N)F$_4$PP)Cu are not observed in the NMR spectrum. This is a common phenomenon for Cu(II) porphyrins and is probably due to excessive line broadening caused by efficient electron relaxation.[24] However, an intense peak is observed at 3.18 ppm for (T(*p*-Me$_2$N)F$_4$PP)Cu and is due to the dimethylamino group on the four phenyl rings of the complex. Thus, all of the NMR data are self-consistent and agree with the formation of (T(*p*-Me$_2$N)F$_4$PP)H$_2$ and (T(*p*-Me$_2$N)F$_4$PP)M from (TF$_5$PP)H$_2$ in DMF.

Summary. The ultimate product in the metalation of (TF$_5$PP)H$_2$ is dependent upon the solvent utilized. A metalation carried out in CH$_3$CN, CHCl$_3$, or toluene leads to the expected (TF$_5$PP)M, but attempts to carry out the same reaction in acetic acid lead only to porpholactone or porphodilactone derivatives.[13] On the other hand, only (T(*p*-Me$_2$N)F$_4$PP)M complexes are obtained as final products in DMF. A replacement of the *p*-F group on (TF$_5$PP)H$_2$ will also occur in the absence of a metal salt and results in the quantitative formation of (T(*p*-Me$_2$N)F$_4$PP)H$_2$.

Finally, it should be noted that the dimethylamino derivatives discussed in this paper provide the first examples for substituted tetraphenylporphyrins where the four phenyl rings contain both electron-withdrawing and electron-donating substituents. The chemical reactivity and electrochemistry of these complexes are currently under investigation.

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Registry No. DMF, 68-12-2; (TF$_5$PP)Co, 129707-77-3; (T(*p*-Me$_2$N)F$_4$PP)Co, 129707-79-5; (T(*p*-Me$_2$N)F$_4$PP)Ni, 129707-80-8; (T(*p*-Me$_2$N)F$_4$PP)Cu, 129707-81-9; (T(*p*-Me$_2$N)F$_4$PP)H$_2$, 129707-76-2; (TF$_5$PP)H$_2$, 25440-14-6.

Supplementary Material Available: Tables of data collection parameters, atomic, hydrogen, and planar atomic coordinates, anisotropic thermal parameters, all intramolecular bond lengths and angles, and molecular packing diagrams (27 pages); listings of observed and calculated structure factors (37 pages). Ordering information is given on any current masthead page.

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