in chloroform. NMR solutions of Zn(II)[14]12eneN$_4$(amine) in chloroform-d_1 slowly decompose (hours) to give the dideuterated form of the ligand, D$_2$[14]12eneN$_4$, and a white solid (possibly $ZnCl_2$).

Both the manganese and zinc complexes are sensitive to alkylating agents. Addition of excess CH_3X, where X is I^- and FSO_3^-, to benzene solutions containing the complexes leads to their destruction. However, the only alkylated product which could be identified from the reaction mixture was $[CH_3NR_3]X$. Attempts to isolate the alkylated form of the ligand lead to hygroscopic yellow solids which could not be characterized. The compounds are easily decomposed by aqueous strong mineral acids, e.g., HCl and $HClO_4$. Unlike the Mn(III) derivatives addition of Et_3N will not restore the original complex. However, if anhydrous HSO_3CF_3 is added to acetonitrile suspensions of the compounds under nitrogen a dissolution accompanied by a color change occurs. Addition of triethylamine results in the regeneration of M(II)[14]12eneN$_4$(amine) (eq 2).

The synthesis and properties of manganese complexes containing other unsaturated tetraaza and mixed N–O donor ligands will be subsequently reported.

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Registry No. H$_2$[14]12eneN$_4$, 56276-51-8; Zn(II)[14]12eneN$_4$(N(Et)$_3$), 56943-15-8; Zn(II)[14]12eneN$_4$(N(*n*-Pr)$_3$), 56943-16-9; Mn(II)[14]12eneN$_4$(N(Et)$_3$), 56943-17-0; Mn(II)[14]12eneN$_4$(N(*n*-Pr)$_3$), 56943-18-1; Mn(III)[14]12eneN$_4$(Cl), 56943-19-2; Mn(III)[14]12eneN$_4$(Br), 56943-20-5; Mn(III)[14]12eneN$_4$(NCS), 56943-21-6; Mn(III)[14]12eneN$_4$(N$_3$), 56943-23-8; Mn(III)(acac)$_2$Cl, 51197-21-8; Mn(III)(acac)$_2$Br, 51147-59-2; Mn(III)(acac)$_2$(NCS), 52242-31-6; Mn(III)(acac)$_2$(N$_3$), 52242-29-2.

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Carbon-13 Nuclear Magnetic Resonance of Substituted Tetraphenyl Porphyrins and Their Complexes with Ruthenium, Indium, and Titanium

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^{13}C NMR spectra of H_2P and MPXY (P = tetrakis(*p*-trifluoromethylphenyl)porphyrin, tetrakis(*p*-isopropylphenyl)porphyrin, and tetrakis(*o*-tolyl)porphyrin, M = Ru, X = CO, Y = tetrahydrofuran, 4-*tert*-butylpyridine, or CO; M = In, X = Cl; M = Ti, X = O; P = octaethylporphyrin, M = Ru, X = CO, Y = tetrahydrofuran; M = In, X = Cl) and RuPX$_2$ (P = tetrakis(*p*-trifluoromethylphenyl)porphyrin), X = trimethyl phosphite and *tert*-butyl isocyanide) are reported and interpreted. Chemical shift differences for nonequivalent sites and ring current effects are compared for ^1H and ^{13}C NMR spectra. Significant dependence of porphyrin chemical shifts on the metal is observed.

Introduction

Recently, increasing effort has been applied to understanding and using ^{13}C NMR to elucidate the chemistry of porphyrins and metalloporphyrins. These studies have concerned the apparent electron delocalization pathway in natural porphyrins,[1] biosynthesis,[2] identification of type isomers,[3] isotropic shifts in paramagnetic iron(III) porphyrins,[4] ring current effects on the porphyrin resonances and on the resonances of other coordinated ligands,[5,6] assignment of spectra of tetrapyrroles,[7] and Cd(II), Hg(II), and Tl(III) complexes of tetraphenylporphyrin.[3c] We now report the ^{13}C NMR spectra of Ru(II), $(TiO)^{2+}$, and In(III) complexes of substituted tetraphenylporphyrins. The compounds chosen for study provide comparison of the relative ^1H and ^{13}C chemical shift differences for sites which are nonequivalent due to restricted phenyl ring rotation.[8] These compounds also provide an indication of the effect of complexed metal on porphyrin chemical shifts.

Experimental Section

Physical Measurements. Infrared spectra were recorded as Nujol or halocarbon mulls on a Perkin-Elmer 710 grating spectrometer. Visible spectra were obtained in chloroform solution on a Beckman Acta V spectrometer. Data are given below with wavelengths in nanometers and log ϵ in parentheses. ^1H NMR spectra were run at power levels well below saturation on a Varian HA-100 spectrometer with the spectrometer locked on the solvent resonance. Unless otherwise noted, ^{1}H chemical shifts are reported in parts per million downfield of tetramethylsilane (TMS) for 1,1,2,2-tetrachloroethane solutions at ambient temperature. ^{13}C NMR spectra were obtained on a Varian CFT-20 ^{13}C pulsed Fourier transform NMR spectrometer operating at 20 MHz with proton noise decoupling and internal deuterium lock. Typically, 4096 data points were taken over a 4-kHz spectral width using a ca. 20° pulse and a ca. 1 sec acquisition time. Samples containing 40–100 mg of compound in 1.5 ml of $CDCl_3$ in 10-mm tubes were run at a probe temperature of ca. 35°. ^{13}C chemical shifts are reported relative to TMS, using the central line of the $CDCl_3$ triplet as a secondary standard with a shift of 77.05 ppm. Positive shifts indicate lower shielding. Shifts are considered accurate to ±0.1 ppm.

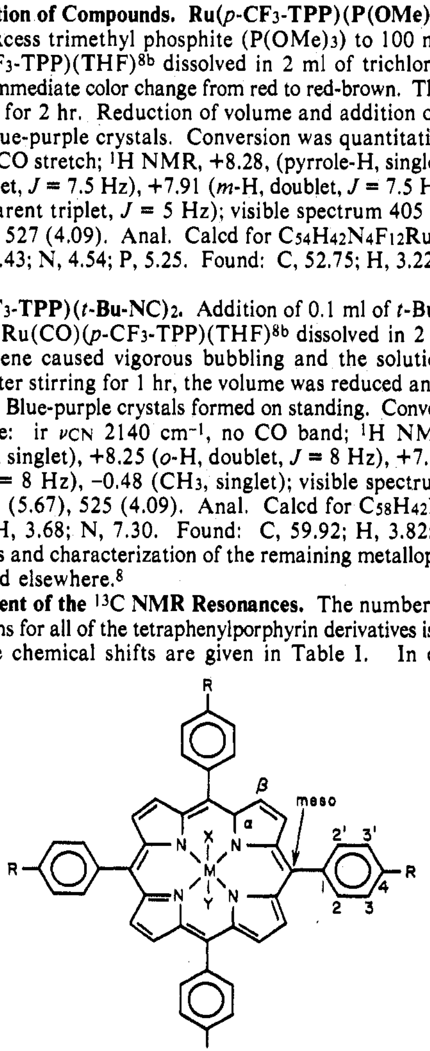
The spectra of the ruthenium carbonyl porphyrins were first run on the compounds as isolated. A second spectrum was obtained in the presence of excess 90% enriched ^{13}CO (Merck). CO exchange affected ^{13}C enrichment of the coordinated CO allowing facile detection of the CO resonance which was difficult to observe in natural abundance.

Preparation of Compounds. Ru(p-CF$_3$-TPP)(P(OMe)$_3$)$_2$.[9] Addition of excess trimethyl phosphite ($P(OMe)_3$) to 100 mg of Ru(CO)(p-CF$_3$-TPP)(THF)[8b] dissolved in 2 ml of trichloroethylene caused an immediate color change from red to red-brown. The solution was stirred for 2 hr. Reduction of volume and addition of heptane afforded blue-purple crystals. Conversion was quantitative: the ir showed no CO stretch; ^{1}H NMR, +8.28, (pyrrole-H, singlet), +8.17 (o-H, doublet, $J = 7.5$ Hz), +7.91 (m-H, doublet, $J = 7.5$ Hz), +0.85 (CH_3, apparent triplet, $J = 5$ Hz); visible spectrum 405 sh (4.71), 426 (5.55), 527 (4.09). Anal. Calcd for $C_{54}H_{42}N_4F_{12}RuO_6P_2$: C, 52.56; H, 3.43; N, 4.54; P, 5.25. Found: C, 52.75; H, 3.22; N, 4.80; P, 5.25.

Ru(p-CF$_3$-TPP)(t-Bu-NC)$_2$. Addition of 0.1 ml of t-Bu-NC[10] to 100 mg of Ru(CO)(p-CF$_3$-TPP)(THF)[8b] dissolved in 2 ml of trichloroethylene caused vigorous bubbling and the solution turned darker. After stirring for 1 hr, the volume was reduced and heptane was added. Blue-purple crystals formed on standing. Conversion was quantitative: ir ν_{CN} 2140 cm^{-1}, no CO band; ^{1}H NMR +8.34 (pyrrole-H, singlet), +8.25 (o-H, doublet, $J = 8$ Hz), +7.94, (m-H, doublet, $J = 8$ Hz), −0.48 (CH_3, singlet); visible spectrum 404 sh (4.66), 421 (5.67), 525 (4.09). Anal. Calcd for $C_{58}H_{42}N_6F_{12}Ru$: C, 60.46; H, 3.68; N, 7.30. Found: C, 59.92; H, 3.82; N, 7.36.

Synthesis and characterization of the remaining metalloporphyrins are reported elsewhere.[8]

Assignment of the ^{13}C NMR Resonances. The numbering of the carbon atoms for all of the tetraphenylporphyrin derivatives is indicated in I. The chemical shifts are given in Table I. In discussing assignments, average values for a porphyrin and its complexes are used; see Table I.



I

H$_2$(p-CF$_3$-TPP) and Complexes. The ^{13}C chemical shifts and C–F coupling constants reported for α,α,α-trifluoromethyltoluene[11a] were used to assign the resonances in the ^{13}C spectra of H$_2$(p-CF$_3$-TPP) and its complexes. The J_{C-F} for CF$_3$, C$_4$, and C$_3$ in the proton-decoupled spectra allow unambiguous assignment of the resonances for these carbons. In H$_2$(p-CF$_3$-TPP) one of the central lines of the quartets assigned to C$_4$ and CF$_3$ is obscured by β-C so the centers of the quartets were estimated using the coupling constants observed for the complexes. The quaternary and nonquaternary carbons are readily distinguished on the basis of intensity differences under the experimental conditions used. The only nonquaternary carbons not assigned on the basis of C–F coupling constants are β-C and C$_2$. The signal at 134.5 ppm is assigned to C$_2$ since it splits into two signals of equal intensity in the complexes. This splitting is expected since C$_2$ and C$_2$' are nonequivalent in these complexes due to restricted rotation of phenyl rings and slow axial ligand exchange.[8] The remaining nonquaternary signal, at 132.1 ppm, is therefore assigned to β-C. Of the quaternary carbon signals, the one due to α-C is easily assigned since it broadens in the free porphyrin due to N–H tautomerism.[3b,12] Two quaternary carbons, C$_1$ and meso-C, remain to be assigned to the signals at 120.7 and 146.0. Based on the chemical shift of the substituted phenyl carbon in biphenyl (141.7 ppm),[13a] styrene (138.2 ppm),[13b] and 3-phenylpyrrole (135.5 ppm)[14] and the 3-C in 3-phenylpyrrole (123.8 ppm),[14] it seems reasonable to assign the signal at 146.0 ppm to C$_1$ and the signal at 120.7 ppm to meso-C. These assignments are considered further in the comparison with the previous assignments for M(TPP), M = Cd(II),[3c] Hg(II),[3c] Tl(III),[3c] and Zn(II).[4b]

H$_2$(p-i-Pr-TPP) and Complexes. Assuming the usual additivity of aromatic ring substituent effects, the phenyl ring resonances of H$_2$(p-i-Pr-TPP) and its complexes can be assigned by comparison with the spectra of substituted benzenes in Table II and the spectra of H$_2$(p-CF$_3$-TPP) and its complexes. The chemical shift differences in ppm between isopropylbenzene and trifluoromethylbenzene (Table II) are C$_a$, 17.9; C$_b$, 1.1; C$_c$, −0.4; C$_d$, −5.8. The proposed assignments in Table I result in the following differences in average chemical shifts between H$_2$(p-i-Pr-TPP) and its complexes and H$_2$(p-CF$_3$-TPP) and its complexes (C$_4$(C$_a$), 18.1; C$_3$(C$_b$), 1.0; C$_2$(C$_c$), 0.1; C$_1$(C$_d$), −6.5), closely paralleling the values for the substituted benzenes. The α-C is readily assigned on the basis of the broadening in the spectrum of the free porphyrin. The only nonquaternary carbon remaining to be assigned, β-C, is assigned on the basis of intensity to the resonance at 132.1 ppm. The remaining signal at 121.9 ppm is meso-C.

H$_2$(o-Me-TPP) and Complexes. The additivity of aromatic ring substituent effects on ^{13}C NMR chemical shifts permits calculation of the shifts expected for H$_2$(o-Me-TPP) using the data in Table II, the assignments made above for H$_2$(p-CF$_3$-TPP) and H$_2$(p-i-Pr-TPP) and their complexes, and the substituent effect of a methyl group.[16] First, the shifts for H$_2$(p-CF$_3$-TPP) and H$_2$(p-i-Pr-TPP) respectively yield the following predictions for H$_2$(TPP): (a) C$_1$, 142.8; C$_2$, 134.3; C$_3$, 127.0; C$_4$, 127.8; and (b) C$_1$, 142.1; C$_2$, 134.8; C$_3$, 126.9; C$_4$, 128.0 ppm. The average of these two sets of predicted shifts agrees closely with the values reported for M(TPP)[3c,4b] except for C$_1$ in Zn(TPP).[4b] If the methyl group is now put on C$_2$', the substituent effect of a methyl group[16] predicts C$_1$, 143.1; C$_2$, 134.5; C$_2$', 143.5; C$_3$, 124.1; C$_3$', 127.7; C$_4$, 127.8. The observed spectra can be assigned with C$_1$, 141.3; C$_2$, 134.0; C$_2$', 139.9; C$_3$, 124.4; C$_3$', 129.4; C$_4$, 128.7 ppm, which is in good agreement with the predictions, particularly if the small upfield shift in C$_1$ and C$_2$' is attributed to a strain contribution. The possible ambiguity between C$_3$' and C$_4$ is resolved by the nonequivalence observed in C$_3$' due to restricted rotation of the phenyl rings.[8] α-C, β-C, and meso-C are assigned by arguments similar to those used for H$_2$(p-i-Pr-TPP) and complexes.

OEP Complexes. The resonances of the octaethylporphyrin complexes were assigned by analogy with the reported spectra of H$_2$(OEP) and Zn(OEP).[3b]

Discussion

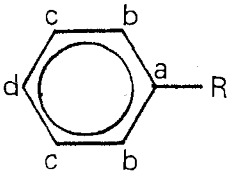
Comparison with Previous Assignments. The assignments given for C$_1$ and meso-C are reversed from those chosen previously for H$_2$(TPP) and Zn(TPP).[4b] Our assignments are based on the following grounds. (1) The assigned chemical shifts of C$_1$ are consistent with chemical shifts in biphenyl,[13a] styrene,[13b] and 3-phenylpyrrole.[14] (2) The variation of the signals at 139–147 ppm, assigned to C$_1$, with changes in phenyl ring substituent is consistent with additivity rules for aromatic rings whereas the signal at 120.7–121.9 ppm, assigned to meso-C, is much less dependent on phenyl ring substituent. (3) The difference in chemical shift between the 3-carbon in pyrrole[13c] and in 3-phenylpyrrole[14] is +16.1 ppm. The chemical shift difference between benzene[13b] and the substituted carbon in biphenyl[13a] is 13.3 ppm. Thus, replacement of a proton on an aromatic ring by a phenyl ring appears to

Table I. ^{13}C NMR of Metalloporphyrins

	Compound	α	β	meso	C_1	C_2	C_2'	C_3	C_3'	C_4	R	L
I	H_2(p-iPr-TPP)	146.8	131.1	120.2	139.6	134.7		124.7		148.2	CH 34.1 CH_3 24.3	
II	In(p-iPr-TPP)Cl	149.6	132.7	121.9	139.1	134.8 (broad)		124.8		148.6	CH 34.1 CH_3 24.3	
III	TiO(p-iPr-TPP)	148.7	132.6	123.8	139.1	134.7		125.0		148.7	CH 34.1 CH_3 24.3	
IV	Ru(CO)(p-iPr-TPP)(py)	143.8	131.8	121.7	140.2	134.2 134.4		124.3 124.6		147.7	CH 34.2 CH_3 24.3	py 144.2, 121.3 CO 180.3
	average of I - IV	147.2	132.1	121.9	139.5	134.6		124.7		148.3		
V	H_2(p-CF_3-TPP)	146.5	131.4	119.1	145.6	134.7		123.9 (3)		130[a]	124.7[a]	
VI	In(p-CF_3-TPP)Cl	149.5	133.1	120.7	145.2	134.4 135.2		124.1 (3.5)		131.0 (32)	124.5 (272)	
VII	TiO(p-CF_3-TPP)	148.4	132.9	122.6	145.2	134.5 134.9		124.1		131.0 (32)	124.7 (268)	
VIII	Ru(CO)(p-CF_3-TPP)(THF)	143.9	132.0	120.9	146.1	134.1 134.5		123.5		130.2 (32)	124.7 (272)	THF 64.2, 22.5 CO 180.1
IX	Ru(p-CF_3-TPP)($P(OMe)_3)_2$	143.8	131.8	120.8	147.0	134.0		123.3 (3)		129.5 (32)	b	CH_3 47.7
X	Ru(p-CF_3-TPP)(t-Bu-NC$)_2$	143.3	131.6	120.2	147.1	134.2		123.4 (3)		129.5 (32)	b	CH_3 29.1
	average of V - X	145.9	132.1	120.7	146.0	134.5		123.7		130.2		
XI	H_2(o-Me-TPP)	146.7	130.8	119.0	141.6	134.0	139.7	124.3	129.3	128.5	21.4	
XII	In(o-Me-TPP)Cl	149.5	132.4	120.6 120.8	141.2	133.5 134.5	139.1 140.8	124.2 124.5	129.3 129.5	128.7	21.1 21.6	
XIII	TiO(o-Me-TPP)	148.5	132.3	122.4 122.6	141.2	133.8 134.2	139.3 140.4	124.3 124.6	129.4 129.6	128.8	21.1 21.9	
	average of XI - XIII	148.2	131.8	121.1	141.3	134.0	139.9	124.4	129.4	128.7		
XIV	Zn(TPP)[c]	150.8	132.5	143.3	121.6	134.9		127.5		128.0		
XV	Cd(TPP)[d]	150.2	131.1	121.0	143.5	134.3		125.7		126.5		
XVI	H_2(OEP)[e]	f	140.9	96.0							CH_2 19.7 CH_3 18.3	
XVII	In(OEP)Cl	146.9	143.4	97.9							CH_2 20.0 CH_3 18.5	
XIX	Ru(CO)(OEP)(THF)	141.7[g]	141.5[g]	98.5							CH_2 19.9 CH_3 18.5	THF 63.0, 21.9 CO 183.
XX	Zn(OEP)[e]	146.7	141.1	96.2							CH_2 19.8 CH_3 18.8	

[a] Estimated by comparison with complexes. β-C obscures part of each quartet in free porphyrin. [b] Not observed. [c] Spectrum in d_5-pyridine/D_2O from reference 4b. [d] Spectrum in $CDCl_3$ with ca. 2 equiv. of pyrrolidine added, from reference 3c. [e] Spectrum in $CDCl_3$ from reference 3b. [f] Not reported. [g] Assignments may be interchanged.

Table II. ^{13}C Chemical Shifts of Substituted Benzenes



R	C_a	C_b	C_c	C_d	Ref
H	128.7	128.7	128.7	128.7	13b
CF_3	131.1	125.4	128.9	131.9	11a
$CH(CH_3)_2$	149.0	126.5	128.5	126.1	15

deshield the substituted carbon by ca. 13–16 ppm. The chemical shift difference of 23–24 ppm between resonances for meso-C in OEP and tetraphenylporphyrin complexes (after allowing for ring substituent effects) would seem more consistent with this expectation than the previously proposed 45-ppm difference.[4b] The assignments are consistent with those reported for M(TPP), M = Cd(II), Hg(II), and Tl(III), on the basis of single-frequency off-resonance decoupling[3c] after completion of this work.

The proposed chemical shift assignments in H_2(*o*-Me-TPP) and complexes for carbons C_2 and C_3 agree with those proposed by Abraham et al. for H_2(*o*-Me-TPP) and its Tl(III) complex.[3c] The assignments for C_3' and C_4 are reversed in this paper relative to those of Abraham et al.[3c] as are the assignments for C_1 and C_2'. In each case the two resonances concerned are within 1 ppm of each other. However, the resonances assigned in this work to C_2' and C_3' in H_2(*o*-Me-TPP) split into pairs of signals in the metal complexes as expected for nonequivalent ortho and meta carbons while the signals for C_1 and C_4 remain unsplit. Thus comparison of the spectrum of the free porphyrin with spectra of the metal complexes removes the possible ambiguity.

Dependence of Chemical Shifts on Coordinated Metal. In NMR studies of paramagnetic metal complexes, calculation of the isotropic shift requires an assumed chemical shift for the same atom in the absence of paramagnetism. Zinc complexes of the same ligand are commonly used as diamagnetic reference compounds. The uncertainty introduced by this assumption can only be estimated by considering the range of shifts for the same ligand atom in complexes with various diamagnetic metals.

The series of compounds reported herein yields information pertinent to estimating the uncertainties in isotropic shift calculations for paramagnetic metalloporphyrins. The ^{13}C chemical shift of the α-C is particularly sensitive to changes in metal ion. For a given substituted tetraphenylporphyrin we observe that different metals cause a range of ca. 6 ppm in the ^{13}C chemical shift of α-C, 1.5 ppm for β-C, 2 ppm for meso-C, 2 ppm for C_1, 0.5 ppm for C_2 or C_3, and 1.5 ppm for C_4. In the ^1H NMR spectra of the same complexes the range of shifts are 1 ppm for pyrrole-H, 0.3 ppm for *o*-H, and 0.2 ppm for *m*-H. Similarly, with OEP complexes, different metals cause a range of ca. 5 ppm in the ^{13}C chemical shift of the α-C, 2 ppm for β-C, 2 ppm for meso-C, 0.2 ppm for CH_2, and 0.3 ppm for CH_3. In the ^{1}H NMR of the same complexes the range of shifts are 0.6 ppm for meso-H, 0.3 ppm for CH_2, and 0.3 ppm for CH_3.

In some cases the range of chemical shifts observed for the few metals studied is as large as the isotropic shifts reported for paramagnetic metalloporphyrins. For example, the isotropic shifts of ^{13}C and ^{1}H resonances in Fe(TPP)$(CN)_2$ reported[4b] relative to Zn(TPP) as diamagnetic reference are listed below, together with the uncertainties calculated using the above ranges of chemical shifts for diamagnetic metalloporphyrins: pyrrole-H, 19.1 (5%); *m*-H, 0.2 (100%); *o*-H, 3.0 (10%); β-C, 41.9 (5%); C_4, −1.0 (67%); C_3, −0.5 (100%); C_2, −33.3 (2%); α-C, 111.0 (5%); meso-C, 24.5 (8%); and C_1, −11.2 (18%). A similar analysis of the isotropic shifts for Fe(TPP)Cl and Fe(OEP)Cl,[17] referenced against the diamagnetic nickel porphyrin, indicates possible uncertainties of up to 10% from this source. Clearly the choice of diamagnetic reference can strongly affect the results of isotropic shift calculations and must be very carefully justified for any particular system. Both the relative range of shifts and the resultant uncertainty in the isotropic shifts are of the same order of magnitude for ^{13}C and ^{1}H NMR spectra.

Carbonyl Resonances. The carbonyl resonance was difficult to detect in the natural abundance spectra. Addition of excess ^{13}CO to the sample tube resulted in substantial isotopic enrichment and the CO resonance became the largest peak in the spectrum. All other resonances in the spectrum of Ru(CO)(*p*-*i*-Pr-TPP)(py) were unchanged by the addition of ^{13}CO. In the spectrum of Ru(CO)(*p*-CF_3-TPP)(THF) separate resonances are observed for the nonequivalent C_2 and C_2' and a broadened multiplet was observed for C_3 and C_3' due to restricted rotation of phenyl rings and slow axial ligand exchange.[8] In the presence of excess ^{13}CO the C_2, C_2' resonances collapse to a single resonance and C_3, C_3' collapse to a quartet (due to coupling to CF_3) indicative of a fast CO exchange from one side of the porphyrin plane to the other. The same spectral changes would be expected for the permutationally equivalent process of phenyl ring rotation, but ring rotation has been demonstrated to be slow on the NMR time scale at room temperature for a range of ruthenium porphyrin complexes.[8] All other resonances are unchanged by CO addition. If the excess CO is then allowed to escape from the sample tube, the CO resonance moves 0.5 ppm to lower shielding relative to the shift observed in the presence of excess CO (179.6 to 180.1 ppm). The remainder of the spectrum is the same as in the presence of excess CO. Apparently CO can compete, on the NMR time scale, with THF for a coordination site in Ru(CO)(*p*-CF_3-TPP)(THF) but cannot compete, on the NMR time scale at 35°, with pyridine for a coordination site in Ru(CO)(*p*-*i*-Pr-TPP)(py). Upon addition of CO to a sample of Ru(CO)(OEP)(THF), the THF resonances are shifted to lower shielding (1.3 ppm for $C_{2,5}$ and 3.0 ppm for $C_{3,4}$). From the ^{1}H NMR spectra it is known that exchange between free and coordinated THF is fast on the NMR time scale at room temperature. The shift in the THF resonances in the presence of excess CO is interpreted as indicating partial displacement of coordinated THF due to dicarbonyl formation. The CO resonance in the presence of excess CO is 2 ppm to greater shielding of the resonance in the absence of excess CO. All other resonances in the spectrum of Ru(CO)(OEP)(THF) are unchanged by the addition of CO.

Separate signals are not observed for mono- and dicarbonyl species, or for uncoordinated ^{13}CO in solution. Apparently, CO exchange is rapid under the conditions of the measurement and the observed shift is a weighted average for the various CO species present. Under the conditions of the spectra, the concentration of free CO in solution was, at most, ca. 3–7% of the concentration of porphyrin.[18] The reported chemical shifts for CO are 182.2 ppm (gas phase)[19a] and 184.6 ppm (D_2O solution).[19b] The ^{13}CO shifts in the Ru(CO)(porphyrin) complexes are in the range 179.6–183 ppm, very close to the shift anticipated for free CO. Thus the relative amount of excess CO in solution would not be expected to have a major effect on the observed average chemical shift. With the caution of these uncertainties it is interesting to note that the larger difference in CO chemical shift in the presence and absence of CO for Ru(CO)(OEP)(L) than for Ru(CO)(*p*-CF_3-TPP)(L) is consistent with considerably greater dicarbonyl formation for the former than for the latter. The difference in behavior of the two ruthenium porphyrins is consistent with the previous findings that the second carbonyl is bound more strongly in $Ru(CO)_2$(OEP) than in $Ru(CO)_2$(*p*-CF_3-TPP).[20]

Previously reported ^{13}C shifts for carbonyl groups bound to ruthenium range from +237.0 ppm for the average CO environment in $(C_5H_5)(CO)\overline{\mathrm{Ru}(\mu\text{-CO})_2\mathrm{Ru}}(CO)(C_5H_5)$[21] to +189.3 and 190.1 ppm in $Ru_3(CO)_9(CMe)H_3$.[22] Other values include +199.7 ppm for the average environment in $Ru_3(CO)_{12}$,[23] 192.1–199.7 ppm in $Ru_3(CO)_9(C_6H_9)H$,[24] and 193.7–198.3 ppm in *cis*-$RuCl_2(CO)_2(L)_2$ where L is a variety of alkyl phosphines.[25] The ^{13}CO resonances in the ruthenium porphyrin complexes appear to be more shielded than those previously reported. The diamagnetic anisotropy of the porphyrin ring may contribute substantially to this difference as discussed below.

Ring Current Effects. The term "ring current shifts" is used to denote those chemical shifts in delocalized molecules, relative to an appropriate reference, attributed to the diamagnetic anisotropy resulting from the electron delocalization. In discussing ring current shifts it is as important to have a reference chemical shift relative to which the ring current shift is calculated, as to have a diamagnetic reference for calculation of paramagnetic isotropic shifts, discussed above. Unfortunately, satisfactory reference shifts for the species studied in this work are not available. In the following discussion comparison will be made to the free ligand, but it must be kept in mind that bonding the ligand to the metal will change the chemical shifts of the ligand nuclei, and that this shift must be accurately accounted for before comparing the observed shifts to a model for ring current effects.

The chemical shifts of the 2,6-C and 3,5-C of pyridine in Ru(CO)(*p*-*i*-Pr-TPP)(py) are 144.2 and 121.3 ppm, respectively, compared with 149.8 and 123.6 ppm in free pyridine.[11b] The −5.6 and −2.3 ppm differences between ^{13}C resonances in free and coordinated pyridine are similar to the −7.64 and −2.39 ppm shift differences for the 2,6-H and 3,5-H in Ru(CO)(OEP)(*t*-Bupy)[26] and −7.09 and −2.08 ppm shift differences for 2,6-H and 3,5-H in Ru(CO)(*p*-CF_3-TPP)(*t*-Bupy).[8] Changes in shift between free and coordinated pyridine resonances in $(py)_2$Co(TPP)Br are −7.80 and −2.08 ppm for 2,6-H and 3,5-H, respectively, and −3.2 and −1.4 ppm for 2,6-C and 3,5-C, respectively.[6] ^{13}C chemical shifts of pyridine coordinated to a metal have been reported for two platinum complexes: in $(CH_3)_2PtBr_2(py)_2$ the ^{13}C shifts for 2,6-C and 3,5-C ($CDCl_3$ solution, ±1.5 ppm) are 151.0 and 125.3 ppm, respectively, and in $(CH_3)_2$Pt(sal=N-CH_3)(py) they are 148.4 and 125.1 ppm, respectively.[27] In these complexes, which do not have the contribution of porphyrin anisotropy to the chemical shift, the 2,6-C resonance shifts in both directions from the shift in uncoordinated pyridine. These complexes are not presented as reasonable reference materials for calculation of ring current shifts in the metalloporphyrins, but rather as indicators of the uncertainties involved.

The methyl carbon resonance of coordinated $P(OMe)_3$ in $Ru(p\text{-}CF_3\text{-}TPP)(P(OMe)_3)_2$ is only −1.2 ppm from the resonance in free $P(OMe)_3$, although in the proton spectrum there is a chemical shift difference of −2.62 ppm between resonances of free and coordinated $P(OMe)_3$. For comparison, note that in $Mo(CO)_5(P(OMe)_3)$, $W(CO)_5(P(OMe)_3)$, and $Mo(CO)_4(P(OMe)_3)_2$ the ^{13}C resonance of coordinated $P(OMe)_3$ is shifted 2.0 to 3.1 ppm downfield with respect to the free ligand.[28] If a similar downfield component to the chemical shift is induced by coordination of $P(OMe)_3$ to the ruthenium porphyrin, the ring current shift is much larger than would be inferred from comparison of the chemical shifts of the methyl carbon in $P(OMe)_3$ and $Ru(p\text{-}CF_3\text{-}TPP)(P(OMe)_3)_2$.

In $Ru(CO)(p\text{-}CF_3\text{-}TPP)(THF)$ the 2,5-C and 3,4-C resonances are −3.7 and −3.3 ppm, respectively, from their positions in free THF.[11c] The corresponding differences in Ru(CO)(OEP)(THF) are −4.9 and −3.9 ppm. The partial displacement of THF from the coordination sphere of Ru(CO)(OEP)(THF) upon addition of CO causes a change in chemical shift of +3.0 ppm for 3,4-C and +1.3 ppm for 2,5-C. The approximate ring current shifts in the ^1H NMR spectra of $Ru(CO)(p\text{-}CF_3\text{-}TPP)(THF)$, using free THF as reference, are −5.4 ppm for 2,5-H and −2.4 ppm for 3,4-H. These results are consistent with previous reports that ring current shifts in ^1H and ^{13}C spectra are of similar magnitude.[6,29] The greater sensitivity of ^{13}C than ^1H to changes in bonding, however, make it more difficult to separate ring current effects from other changes that result from coordination to the ruthenium. Thus, bonding influences on the 2,6-C chemical shift in coordinated THF may account for the lower ratio of apparent 2,5-C:3,4-C (1.1) ring current shifts compared to the 2,5-H:3,4-H (2.25) in $Ru(CO)(p\text{-}CF_3\text{-}TPP)(THF)$.

Even though there are not adequate reference shifts for the determination of ring current shifts for these metalloporphyrin complexes, it is of interest to compare the estimated ring current shifts with calculated values. Among the recent ring current calculations,[30-32] direct application to porphyrins is most readily made using the figures in ref 30. Bond distances were obtained from the x-ray crystal structure of Ru(CO)(TPP)(py)[33] and Ru(CO)(TPP)(EtOH)[34] or estimated from molecular models. The calculated ring current shifts were extrapolated where necessary. The calculated ring current shifts in ppm and observed shifts relative to the free ligands, in parentheses, for *t*-Bupy are *o*-H, 6 (7.1); *o*-C, 6.5 (5.6); *m*-H, 2 (2.1); *m*-C, 2 (2.3); *t*-Bu-H, 1 (0.9–1.03), and for $P(OMe)_3$ C, 2 (3.); H, 1.7 (2.6). This agreement is probably fortuitous, since it is better than the uncertainty in some of the individual values. Extending this treatment to the carbon of the coordinated CO, the calculations[30] extrapolate to an estimated ring current contribution of ca. 10–12 ppm. When this factor is taken into consideration, the ^{13}C shifts of the carbonyl carbon in ruthenium carbonyl porphyrins are consistent with the chemical shifts observed for other Ru–CO units.[21-25]

Chemical Shift Differences between Nonequivalent Sites. In indium chloro, titanyl, and ruthenium carbonyl complexes of substituted tetraphenyl porphyrins slow axial ligand exchange and slow rotation, on the NMR time scale, of the phenyl rings with respect to the plane of the porphyrin result in nonequivalence of the two sides of each phenyl ring.[8] The resulting chemical shift differences between nonequivalent protons[8] are given in Table III along with the ^{13}C nonequivalences for the related carbons, in ppm. Chemical shift differences in the proton resonances are for spectra at ca. 30° except for $TiO(p\text{-}i\text{-}Pr\text{-}TPP)$ and $TiO(p\text{-}CF_3\text{-}TPP)$ where it is necessary to go to 9 and 17°, respectively, to obtain a slow exchange spectrum.[8] All ^{13}C spectra are at ca. 35°.

Table III. Chemical Shift Differences (ppm) in ^1H and ^{13}C NMR Spectra

A. Nonequivalence Arising from Restricted Rotation of Phenyl Rings

Compd	*o*-H[a]	$C_2(C_2')$	*m*-H	$C_3(C_3')$
$In(p\text{-}CF_3\text{-}TPP)Cl$	0.31	0.80	0.08	
$TiO(p\text{-}CF_3\text{-}TPP)$[b]	0.40	0.39 (broad)	0.10	(Broad)
$Ru(CO)(p\text{-}CF_3\text{-}TPP)(THF)$	0.16	0.35	0.04	(Broad)
In(*p*-*i*-Pr-TPP)Cl	0.32	(Broad)	0.06	
TiO(*p*-*i*-Pr-TPP)[c]	0.41		0.07	
Ru(CO)(*p*-*i*-Pr-TPP)(EtOH)	0.12		0.03	
Ru(CO)(*p*-*i*-Pr-TPP)(py)		0.20		0.20

B. Nonequivalence Arising from Isomers in Tetra(*o*-tolyl)porphyrins

Compd	*o*-H[a]	C_2	C_2'	C_2'-CH_3	*o*-CH_3	*m*-H *p*-H[d]	C_3	C_3'
H_2(*o*-Me-TPP)	0.11				0.06	0.25		
In(*o*-Me-TPP)Cl	0.46	1.0	1.7	0.5	0.41	0.20	0.3	0.2
TiO(*o*-Me-TPP)	0.77	0.4	0.4	0.9	0.70	0.40	0.3	0.2

[a] The *o*-H protons are bound to C_2 and C_2'. [b] ^1H spectrum at 17°. [c] ^1H spectrum at 9°. [d] *p*-H and *m*-H have similar shifts and individual resonances are not readily assigned.

For $M(p\text{-}CF_3\text{-}TPP)X$ the chemical shift differences in ppm between C_2 and C_2' in the ^{13}C NMR spectra are up to about a factor of 2 larger than the shift differences between their respective protons (*o*-H and *o*-H') in the ^1H NMR spectra. Shift differences between C_3 and C_3' are not resolvable, due in part to the C–F coupling constant of 3 Hz between $C_3(C_3')$ and the CF_3 group. Nonequivalences in the proton spectra are 0.10 ppm or less.[8] It should also be noted that the ^1H spectra were obtained at 100 MHz and the ^{13}C spectra at 20 MHz and the ^1H spectra were obtained at higher resolution so that small nonequivalences were much more readily detected in the ^1H than in the ^{13}C spectra. The broadening of the C_2 and C_2' resonances in the spectrum of $TiO(p\text{-}CF_3\text{-}TPP)$ is attributed to intermediate rate of rotation of the phenyl rings. Considerable broadening of the ^1H spectra is also observed at ca. 35°.

The ^{13}C spectra of M(*p*-*i*-Pr-TPP)X are considerably less informative concerning nonequivalent phenyl sites than are the ^1H spectra even though the chemical shift differences in the ^1H spectra of M(*p*-*i*-Pr-TPP)X and $M(p\text{-}CF_3\text{-}TPP)X$ are very similar. The observation of a single resonance for C_2 and C_2' in TiO(*p*-*i*-Pr-TPP) is not surprising in view of the ca. 40° coalescence temperature for the ortho protons.[8] It is interesting to note that the ^{13}C chemical shift differences between C_2 and C_2' and between C_3 and C_3' in Ru(CO)(*p*-*i*-Pr-TPP)(py) are approximately equal, whereas in the ^1H NMR of a large range of complexes the nonequivalence between *o*-H protons was several times larger than between *m*-H protons.

Striking differences are found between the CH_3 resonances of H_2(*o*-Me-TPP) and M(*o*-Me-TPP)X. In the ^1H NMR spectrum of H_2(*o*-Me-TPP) the various isomers give rise to five distinguishable CH_3 resonances, but in the ^{13}C spectrum only one CH_3 resonance is seen. The spectra of the M(*o*-Me-TPP)X complexes, however, show ten CH_3 resonances in two major groupings in the ^1H spectrum and two CH_3 resonances in the ^{13}C spectrum. Similar behavior is observed for the resonances of the ring carbons and their attached protons, except that in this case the ^{13}C spectra are more easily interpreted due to the complicated coupling in the ^1H spectra. These observations imply that the chemical shifts of the *o*-tolyl ring resonances are dependent primarily upon the orientation of the nucleus relative to the axial ligand on the metal.

Thus there appear to be similarities although not exact correspondance in chemical shift differences (in ppm) between nonequivalent sites in the ${}^{13}C$ and ${}^{1}H$ spectra. However, the factor of 5 difference in frequency of observation at comparable field strengths for the two nuclei makes it easier to observe small differences in the ${}^{1}H$ spectra than in the ${}^{13}C$ spectra for those cases where the proton–proton coupling pattern is relatively simple.

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Thiolato Sulfur as an Electron-Transfer Bridge. The Chromium(II)-Catalyzed Aquation of Thiolatobis(ethylenediamine)chromium(III) Complexes in Aqueous Perchloric Acid Media

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The rates of the chromium(II) reductions of the $[Cr(en)_2(SCH_2COO)]^+$, $[Cr(en)_2(SC_6H_4COO)]^+$, $[Cr(en)_2(SCH_2CH_2NH_2)]^{2+}$, and $[Cr(en)_2(OOCCOO)]^+$ ions have been measured in aqueous perchloric acid media. All reactions proceed by inner-sphere electron transfer. Reduction of the mercaptoacetato and 2-mercaptobenzoato complexes is strongly catalyzed by acid, whereas reduction of the 2-mercaptoethylamine and oxalato complexes is essentially independent of acid. The acid-catalyzed redox path is interpreted in terms of a proton-induced cis nonbridging ligand effect. Rates of the title reactions are compared to the rates of chromium(II) reduction of the analogous thiolatobis(ethylenediamine)cobalt(III) complexes, and arguments are presented which indicate that the remarkable bridging efficiency reported for thiolato sulfur in Cr(II)–Co(III) reactions does not carry over to the analogous Cr(II)–Cr(III) reactions. It is suggested that this kinetic difference may arise from the fact that thiolato sulfur induces a ground state trans effect in the cobalt(III) complexes, but not in an analogous chromium(III) complex.

Introduction

The remarkable ability of low-valent sulfur to mediate electron transfer from chromium(II) to cobalt(III) was first noted by Bennett[2] for thiolato sulfur. Thiocyanato sulfur was shown to also efficiently bridge electron transfer from chromium(II) to cobalt(III),[3] as well as from uranium(III) to chromium(III),[4] but a study on electron transfer from cobalt(II) (as $[Co(CN)_5]^{3-}$) to cobalt(III) was inconclusive.[5] In an effort to determine if the unusually great bridging efficiency of thiolato sulfur in Cr(II)–Co(III) reactions extends to other redox systems, we have prepared, characterized, and quantified the acid-catalyzed aquation of thiolatobis(ethylenediamine)chromium(III) complexes[6] which are analogous to the thiolatobis(ethylenediamine)cobalt(III) complexes