Metalloradical Chemistry of Cobalt(II) Porphyrins. The Syntheses, Structure, and Reactivity of Triphenyltin(II)- and Trihalomethylcobalt(III) Octaethylporphyrin

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Stannanes R_3SnH (R = n-Bu, Ph) reacted with $Co^{III}(OEP)CH_3$ or $Co^{II}(OEP)$ to afford $Co^{III}(OEP)SnR_3$ and CH_4 or H_2, respectively. $Co^{III}(OEP)SnR_3$ was more efficiently prepared by reaction of $Co^{I}(OEP)^-$ with R_3SnCl. $Co^{III}(OEP)SnPh_3$, $C_{54}H_{59}CoN_4Sn$, crystallized in the triclinic space group $P\bar{1}$ ($Z = 2$) with unit cell dimensions $a = 12.124(5)$ Å, $b = 14.700(5)$ Å, $c = 15.221(7)$ Å, $\alpha = 109.56(4)°$, $\beta = 91.44(5)°$, $\gamma = 113.27(1)°$, and $V = 2308.4(1.8)$ Å^3 at 295(2) K. The structure resembled that of five-coordinate alkylcobalt(III) porphyrin complexes with a square-pyramidal Co atom displaced 0.077 Å out of the porphyrin plane toward Sn and a Co−Sn bond length of 2.510(2) Å. The bond dissociation energy of the Co−Sn bond was considerably larger than that of the Co−C bond in alkylcobalt(III) porphyrin complexes. $Co^{III}(OEP)SnPh_3$ was air stable in solution and decomposed by homolysis slowly at 120 °C in toluene. The Co−Sn bond was rapidly cleaved, though, when oxidized by I_2 or by electrochemical means. In contrast, the Co−C bonds in $Co^{III}(OEP)CX_3$ (X = Cl, Br, I) were substantially weaker than in the Co−C bond in alkylcobalt(III) porphyrin complexes and weakened progressively with heavier halogens. $Co^{III}(OEP)CX_3$ complexes were prepared by reaction of $Co^{I}(OEP)^-$ with CX_4 (X = Cl, Br) or by reaction of $Co^{II}(OEP)$ with $CBrCl_3$ or CX_4 (X = Br, I). The reaction of $Co^{I}(OEP)^-$ with CX_4 (X = Cl, Br, I) also afforded small amounts of $Co^{III}(OEP)CHX_2$ complexes, which were obtained in greater yield by reaction of $Co^{I}(OEP)^-$ with CHX_3. The substitution of one hydrogen for a halogen stabilized the $Co^{III}(OEP)CHX_2$ complexes relative to the corresponding $Co^{III}(OEP)CX_3$ complexes.

Cobalt porphyrins and rhodium porphyrins are isoelectronic and have the same ranges of accessible formal oxidation states. Although the porphyrin compounds of the two metals have similarities in their chemistries, the differences are particularly remarkable.

Rhodium forms stable alkyl[1] and hydrido[2,3] Rh(III) porphyrin complexes. Low spin d^7 ($S = {}^1/_2$) metalloradical Rh(II) porphyrin complexes are produced by photolysis of the alkyl complexes,[4] and can be obtained from the hydrido complexes by thermal loss of H_2,[2] controlled oxidation,[3] or hydrogen atom abstraction.[5] Rh(II) porphyrin complexes are in equilibrium with diamagnetic Rh−Rh bonded dimers.[6] The hydrido rhodium(III) and Rh(II) dimer complexes both react via radical mechanisms[7] to insert small unsaturated molecules including CO,[8−11] O_2,[12,13] alkenes,[2,7,14,15] and isocyanides.[9] Rh(II) porphyrins activate alkyl C−H bonds in alkylaromatics and methane,[16−18] H−H bonds in H_2,[9,19] and E−H bonds in silane and stannanes (E = Si and Sn, respectively).[20]

Cobalt forms stable alkyl Co(III) porphyrin complexes,[21−23] but no hydrido Co(III) porphyrin complexes have been isolated to date. Evidence, though, suggests the hydrido complexes are transient intermediates in several reactions.[24−29] Although Co(II) porphyrins are formally metalloradicals, their reactivity is

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not particularly radical-like. They are invariably mononuclear, $S = {}^1/_2$ complexes. Co(II) porphyrins do not react with oxygen in the absence of anions that could serve as an axial ligand. In addition, they do not insert small unsaturated molecules or abstract chlorine atoms from chlorinated solvents. However, Co(II) porphyrins do recombine with alkyl radicals to afford alkyl Co(III) porphyrins.[30]

Recently, we investigated the effect of compounds that trap alkyl radicals on the alkyl exchange reactions of cobalt porphyrins, eq 1.[31] The initial control experiments showed that

$$\mathrm{R{-}Co^{III}(P) + Co^{II}(P^*) \rightleftharpoons Co^{II}(P) + R{-}Co^{III}(P^*)} \quad (1)$$

both $\mathrm{Co^{III}(OEP)CH_3}$ and $\mathrm{Co^{II}(OEP)}$ reacted directly with organotin hydrides and bromotrichloromethane to afford previously unknown diamagnetic cobalt(III) porphyrin compounds that had distinctive ^{1}H chemical shifts for the *meso*-protons. This paper reports the characterization, reactivities, and alternative synthetic approaches to several new triaryltin- and trihalomethylcobalt(III) porphyrin complexes that were formed in these reactions in which Co(II) porphyrins appear to display radical reactivity. $\mathrm{Co^{III}(OEP)SnPh_3}$ has a remarkably strong Co−Sn bond. In contrast, the Co−C bonds in $\mathrm{Co^{III}(OEP)CX_3}$ complexes are weak.

Experimental Section

Materials and Methods. All reactions, recrystallization, and sample manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques or in a Vacuum Atmospheres Co. Drybox unless noted otherwise. $\mathrm{Co^{II}(OEP)}$,[32] $\mathrm{Co^{II}(TTP)}$,[32] $\mathrm{Co^{III}(OEP)CH_3}$,[22,33] and $\mathrm{Co^{III}(OEP)X}$ (X = Cl, Br, I)[34] were prepared by literature methods. We found, though, that preparation of $\mathrm{Co^{III}(OEP)I}$ by direct reaction of $\mathrm{Co^{II}(OEP)}$ and $\mathrm{I_2}$ was more convenient than the literature method of reaction of $\mathrm{Co^{II}(OEP)}$ with HI in methanol in air. Alkyl, $\mathrm{R_3Sn}$, and halomethyl cobalt(III) porphyrin complexes were handled under subdued light. Carbon tetrahalide, haloform, tin hydride, and tin chloride reagents were obtained from Aldrich or Fisher Scientific and were used as received. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl. Other solvents were refluxed over $\mathrm{CaH_2}$ or an appropriate drying agent and then distilled. $\mathrm{CDCl_3}$ and $\mathrm{CD_2Cl_2}$ were passed through a bed of neutral grade I alumina and deoxygenated immediately prior to use. Other deuterated solvents were rigorously deoxygenated but otherwise used as received.

^{1}H NMR spectra (270.17 MHz) were recorded on a JEOL Eclipse 270 spectrometer. Most reactions were run in deuterated solvents in an NMR tube. The porphyrin complex typically had a concentration of 3×10^{-3} M. For reactions at elevated temperature, the NMR tube was heated in a temperature control bath between observations of the NMR spectra, which were recorded at a nominal temperture of 21 °C. High-pressure reactions were run in a small Fisher Porter type bottle and aliquots were removed at intervals for observations. Headspace gases were analyzed on a Hewlett-Packard 5890A gas chromatograph. The valve system for sampling as well as columns and conditions employed were described previously.[35] Absorption spectra were recorded on a Perkin-Elmer Lambda 4C spectrophotometer. CV measurements were peformed with a BAS CV-50W potentiostat in a cell with an Au working electrode, Pt auxiliary electrode, and Ag/Ag$^+$ reference electrode. The $\mathrm{CH_2Cl_2}$ solution was 0.1 M in TBAP. The potential of the ferrocene/ferrocenium complex was +0.180 V vs the Ag/Ag$^+$ reference.

Table 1. Experimental Data for the X-ray Crystal Structure of $\mathrm{Co^{III}(OEP)SnPPh_3}$

empirical formula	$\mathrm{C_{54}H_{59}CoN_4Sn}$
cryst syst	triclinic
space group	$P\bar{1}$
a, Å	12.124(5)
b, Å	14.700(5)
c, Å	15.221(7)
α, deg	109.56(4)
β, deg	91.44(5)
γ, deg	113.27(1)
V, Å^3	2308.4(1.8)
Z	2
fw, amu	941.67
ρ_{calc}, g/cm^3	1.354
cryst size	0.09 × 0.22 × 0.26 mm
μ, cm^{-1}	9.40
T, °C	22(2)
λ, Å	0.710 73
θ range of measd reflns, deg	2.14−22.53
index ranges	$0 < h < 13$, $-14 < k < 13$, $-16 < l < 16$
no. of reflns collcd	6113
no. of indep reflcns	5789 ($R_{\mathrm{int}} = 0.0480$)
refinement method	full-matrix least-squares on F^2
data/restraints/parameters	5185/0/549
goodness-of-fit on F^2	0.998
final R indices^a [$I > 2\sigma(I)$]	R1 = 0.0476, wR2 = 0.0809
R indices (all data)	R1 = 0.0982, wR2 = 0.0983
largest diff. peak and hole (e A^{-3})	0.447 and −0.348

[a] The discrepancy indices were calculated from the expressions $\mathrm{R1} = \sum||F_o| - |F_c||/\sum|F_o|$ and $\mathrm{wR2} = [\sum(w_i(F_o^2 - F_c^2)^2)/\sum(w_i(F_o^2)^2)]^{1/2}$, and the standard deviation of an observation of unit weight (GOF) is equal to $[\sum(w_i(F_o^2 - F_c^2)^2)/(n - p)]^{1/2}$, where n is the number of reflections and p is the number of parameters varied during the last refinement cycle.

Synthesis of $\mathrm{Co^{III}(OEP)SnPh_3}$. A solution of 50 mg of $\mathrm{Co^{II}(OEP)}$ (8.5×10^{-5} mol) in 15 mL of THF was stirred over 2.0 g of 2% sodium amalgam for 20 h. The solution was filtered and added to 163 mg of $\mathrm{Ph_3SnCl}$ (5 equiv, 4.25×10^{-4} mol). The resulting solution was stirred for 1 h, the solvent was removed under vacuum, and the crude product was purified by column chromatography on neutral grade I alumina using 1:3 methylene chloride/hexane as the eluant. Recrystallization from toluene afforded 54 mg of reddish purple crystals (68% yield). ^{1}H NMR ($\mathrm{CDCl_3}$): 1.77 (t, 24 H, $\mathrm{CH_3}$, J = 7.4 Hz), 3.81 (m, 16 H, $\mathrm{CH_2}$), 4.57 (d, 6H, *o*-H, $^3J_{\mathrm{HH}}$ = 7.0 Hz, $^3J_{\mathrm{SnH}}$ = 43.7 Hz), 6.47 (t, 6H, *m*-H, J = 7.0 Hz), 6.76 (t, 3H, *p*-H, J = 7.0 Hz), 9.72 (s, 4H, meso CH). ^{1}H NMR ($\mathrm{C_5D_5N}$): 1.86 (t, 24 H, $\mathrm{CH_3}$), 3.90 (m, 16 H, $\mathrm{CH_2}$), 4.99 (d, 6H, *o*-H), 6.61 (t, 6H, *m*-H), 6.89 (t, 3H, *p*-H), 10.02 (s, 4H, meso CH). UV−vis ($\mathrm{C_6D_6}$), (λ_{max} (nm), ϵ (10^4 M^{-1} cm^{-1})): 382 (8.0), 407 (sh), 518 (sh), 547 (2.2).

X-ray Structural Analysis of $\mathrm{C_{54}H_{59}CoN_4Sn}$, $\mathrm{Co^{III}(OEP)SnPh_3}$. A crystal of $\mathrm{Co^{III}(OEP)SnPh_3}$ was sealed under nitrogen in a glass capillary tube and then optically aligned on the goniostat of a Siemens P4 automated X-ray diffractometer. The reflections used for the unit cell determination were located and indexed by the automatic peak search routine provided with XSCANS.[36] The final lattice parameters and orientation matrix for the triclinic unit cell were calculated from a nonlinear least-squares fit of the orientation angles of 24 reflections ($20 < 2\theta < 25°$). The refined lattice parameters and other pertinent crystallographic information are summarized in Table 1.

Intensity data were measured with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) and variable ω scans (4−10°/min).

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(36) XSCANS (version 2.0) is a diffractometer control system developed by Siemens Analytical X-ray Instruments, Madison, WI.

Table 2. Selected and Average Bond Lengths (Å) and Bond Angles (deg) for $Co^{III}(OEP)SnPh_3$[a]

Co−Sn	2.510(2)	Sn−C(37)	2.171(7)
Sn−C(43)	2.151(7)	Sn−C(49)	2.160(7)
Co−N(1)	1.962(5)	Co−N(2)	1.975(5)
Co−N(3)	1.963(5)	Co−N(4)	1.962(5)
$C_{Ph}-C_{Ph}$[b]	1.376(3)	Co−Ct[c]	0.077
$N-C_a$	1.388(3)	C_a-C_m	1.370(2)
C_a-C_b	1.441(4)	C_b-C_b	1.354(2)
C_b-CH_2	1.511(4)	CH_2-CH_3	1.499(7)
Co−Sn−C(37)	121.1(2)	Co−Sn−C(43)	113.0(2)
Co−Sn−C(49)	108.8(2)	C(37)−Sn−C(43)	101.0(2)
C(37)−Sn−C(49)	101.4(3)	C(43)−Sn−C(49)	110.8(3)
N(1)−Co−Sn	90.6(2)	N(2)−Co−Sn	88.8(2)
N(3)−Co−Sn	93.43(14)	N(4)−Co−Sn	96.1(2)
$c-N_{eq}-Co-N_{eq}$	89.9(1)	$t-N_{eq}-Co-N_{eq}$	175.5(4)
$Co-N-C_a$	128.0(1)	C_a-N-C_a	104.0(2)
$N-C_a-C_m$	123.9(2)	$N-C_a-C_b$	111.2(2)
$C_m-C_a-C_b$	124.9(4)	$C_a-C_m-C_a$	126.0(5)
$C_a-C_b-C_b$	106.8(4)		

[a] For bonds and angles that are averages, the ESDs in parentheses were calculated for averages of populations assuming idealized D_{4h} symmetry for the porphyrin and C_6 symmetry for the phenyl rings. ESDs of individual distances were typically 0.009 Å for the porphyrin core C−C and C−N bonds. ESDs of individual angles were typically 0.6° or less. [b] Abbreviations: Ph, phenyl; eq, equatorial; ax, axial; a, pyrrole α-carbon; b, pyrrole *β*-carbon; m, *meso*-carbon; Ct, center. [c] Displacement of Co atom from the least-squares plane of the four equatorial nitrogen atoms.

Background counts were measured at the beginning and at the end of each scan with the crystal and counter kept stationary. The intensities of three standard reflections were measured after every 100 reflections and did not vary significantly during data collection. The raw data were corrected for Lorentz−polarization effects.

Initial coordinates for the non-hydrogen atoms were determined by a combination of heavy atom and direct methods performed with the algorithms provided in SHELXTL-IRIS operating on a Silicon Graphics Iris Indigo workstation. The hydrogen atom positions were idealized with isotropic temperature factors set at 1.2 times that of the adjacent carbon. The positions of the methyl hydrogens were optimized by a rigid rotating group refinement with idealized tetrahedral angles. Full-matrix least-squares refinement with SHELXL-93,[37] based upon the minimization of $\sum w_i|F_o^2 - F_c^2|^2$ with weighting given by the expression $w_i^{-1} = [\sigma^2(F_o^2) + (0.0310P)^2]$ where $P = (\mathrm{Max}(F_o^2,0) + 2F_c^2)/3$, converged to give final discrepancy indices[38] of R1 = 0.0476, wR2 = 0.0809 for the 3835 reflections with $I > 2\ \sigma(I)$ and an overall GOF value = 0.998. Selected and average interatomic distances and bond angles are listed in Table 2.

Results

Formation of $Co^{III}(OEP)SnR_3$ (R = n-Bu, Ph). Reaction of $Co^{III}(OEP)CH_3$ with excess tributyltin hydride in benzene solution resulted in a decrease in the intensities of the ^{1}H NMR singlets of the *meso*-protons and axial methyl group of $Co^{III}(OEP)CH_3$ at 10.24 and −4.51 ppm, respectively. Concurrently, in regions not obscured by the large excess of tributyltin hydride, two new upfield multiplets at −2.31 and −0.63 ppm, a new singlet at 10.03 ppm, and changes in the multiplet due to the diastereotopic methylenes of the OEP ethyl groups appeared. The new upfield multiplets imply the presence of an alkyl group situated in the shielding region above the ring current of the porphyrin. However, the appearance and shifts of these multiplets are distinct from those of the known $Co^{III}(OEP)C_4H_9$, as is the shift of the *meso*-proton singlet.[33] Analogous changes in the ^{1}H NMR spectrum were observed during the reaction of $Co^{III}(OEP)CH_3$ with triphenyltin hydride. The disappearance of the *meso*-proton and axial methyl singlets were accompanied by the appearance of a new singlet at 9.91 ppm and three new multiplets, upfield of the triphenyltin hydride phenyl peaks, at 4.92, 6.49, and 6.74 ppm. The doublet at 4.92 ppm clearly showed satellites due to coupling to Sn isotopes. Thus, the new species formed are $Co^{III}(OEP)SnR_3$ (R = Ph, *n*-Bu).

The rate of reaction of $Co^{III}(OEP)CH_3$ with triphenyltin hydride appears comparable to that with tributyltin hydride. For millimolar solutions of the porphyrin complex, reactions go to completion in a reasonable time when 50 or more equivalents of hydride are employed (roughly 5 h for 100 equiv and 24 h for 50 equiv). Smaller excesses of the hydride lead to extended reaction times and/or incomplete reaction. The reactions are also noticably slower if $Co^{II}(OEP)$ impurities are present.

The $Co^{III}(OEP)SnR_3$ complexes were also produced by reaction of $Co^{II}(OEP)$ with excess tin hyride in benzene. The reactions were much slower than those with $Co^{III}(OEP)CH_3$. Less than 50% conversion occurred after 2 days of reaction with 100 equiv of tributyltin hydride. Significantly less conversion to product occurred after 2 days of reaction with 100 equiv of triphenyltin hydride. The reactions with $Co^{II}(OEP)$ were also less selective. When 50 equiv or less of tributyltin hydride was used, the reaction also afforded $Co^{III}(OEP)C_4H_9$. The ratio of this product to $Co^{III}(OEP)Sn(C_4H_9)_3$ increased as the excess of hydride decreased.

Analysis of headspace gases by gas chromatography identified other reaction products. Methane was detected in the headspace of the reactions of $Co^{III}(OEP)CH_3$ with the tin hydrides. Significant quantities of H_2 were detected in the headspace after $Co^{II}(OEP)$ was reacted with 100 equiv of triphenyltin hydride for 2 days in the dark. No H_2 was detected in the headspace when either $Co^{II}(OEP)$ or $HSnPh_3$ in benzene was allowed to stand for 2 days. The two reactions can be represented as eqs 2 and 3. Neither CH_4 nor H_2 was determined quantitatively.

$$Co^{III}(OEP)CH_3 + R_3SnH \rightarrow CH_4 + Co^{III}(OEP)SnR_3 \quad (2)$$

$$Co^{II}(OEP) + R_3SnH \rightarrow {}^1/_2H_2 + Co^{III}(OEP)SnR_3 \quad (3)$$

Thus, the complete mass balance of the reactions has not been established, and processes other than eq 2 and 3 cannot be excluded.

The large excesses of $HSnR_3$ complicates the isolation and purification of the $Co^{III}(OEP)SnR_3$ complexes. To obviate this problem, we approached the synthesis of the complexes by reaction of $Co^I(OEP)^-$ with Ph_3SnCl or $(C_4H_9)_3SnCl$, eq 4. Both

$$Na[Co^I(OEP)] + R_3SnCl \rightarrow NaCl + Co^{III}(OEP)SnR_3 \quad (4)$$

reactions afforded complete conversion with 5 or fewer equiv of the tin halide. No difficulties were encountered in the purification of $Co^{III}(OEP)SnPh_3$. In contrast, attempts to purify $Co^{III}(OEP)Sn(C_4H_9)_3$ by chromatography led to partial conversion to $Co^{III}(OEP)C_4H_9$. Thus, only the structure and properties of $Co^{III}(OEP)SnPh_3$ were investigated further.

Structure of $Co^{III}(OEP)SnPh_3$. The ORTEP drawing of the structure of $Co^{III}(OEP)SnPh_3$ is shown in Figure 1. The structure is analogous to those of five-coordinate Co(III) alkyl

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(37) SHELXL-93 is a FORTRAN-77 program (Professor G. Sheldrick, Institut für Anorganische Chemie, University of Göttingen, D-37077, Göttingen, Germany, 1993) for single-crystal X-ray structural analyses.

(38) The discrepancy indices were calculated from the expressions $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $wR2 = [\sum(w_i(F_o^2 - F_c^2)^2)/\sum(w_i(F_o^2)^2)]^{1/2}$ and the standard deviation of an observation of unit weight (GOF) is equal to $[\sum(w_i(F_o^2 - F_c^2)^2)/(n - p)]^{1/2}$, where *n* is the number of reflections and *p* is the number of parameters varied during the last refinement cycle.

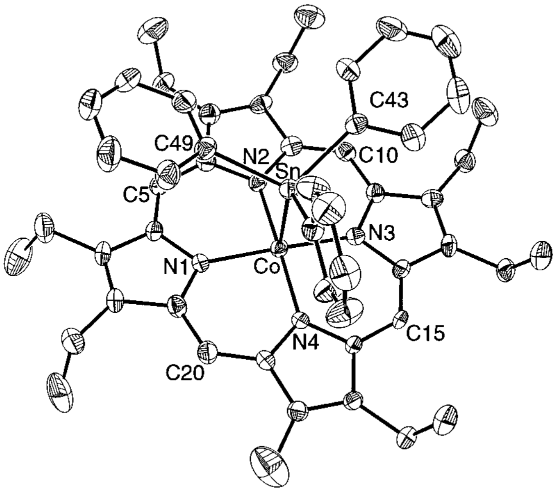

Figure 1. ORTEP diagram of the molecular structure of Co^{III}(OEP)$SnPh_3$, $C_{54}H_{59}CoN_4Sn$. For sake of clarity, thermal ellipsoids are scaled to enclose 30% probability and the H atoms and the label for the *ipso*-phenyl carbon atom C37 are omitted. C35 is hidden behind C36.

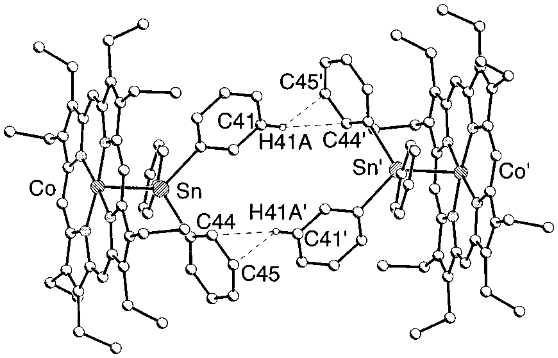

Figure 2. Edge-to-face π interaction in Co^{III}(OEP)$SnPh_3$. Atoms of the inversion related molecule are designated by appending a prime symbol (′) to their labels. H atoms not involved in the interaction are omitted for sake of clarity.

porphyrin complexes. Co^{III}(OEP)$SnPh_3$ has average bond lengths and angles, Table 2, that are typical of porphyrins and indistinguishable from those of Co^{III}(OEP)CH_3 and Co^{III}(OEP)Et.[33,39] The porphyrin skeleton is nearly planar. The largest displacement from the 24-atom plane is 0.143 Å for C(2), but typical displacements are only about 0.05 Å. The four nitrogen atoms are coplanar within ±0.008 Å. The square pyramidal cobalt atom lies 0.077 Å above this plane, toward the axial $SnPh_3$ group. This displacement is somewhat smaller than in the alkyl complexes.

The most unusual aspect of the structure is the axial $SnPh_3$ group. The Co−Sn bond length of 2.510(2) Å, which is presumed to be a single bond, cannot be directly compared to other bonds of this type. A search of the Cambridge Structural Database retrieves 29 other structures containing 47 Co−Sn bonds involving 4-coordinate Sn, whose lengths range from a minimum of 2.441 Å to a maximum of 2.679 Å with a mean of 2.562 Å.[40] If the search is restricted to Co−$SnPh_3$ fragments, five examples with a Co−Sn range of 2.546 to 2.598 Å and mean of 2.577 Å are found. However, all of the compounds nominally involve Co(I) in carbonyl or organometallic fragments rather than Co(III). The Co−Sn bond vector is canted slightly off the normal of the N_4 plane toward N(2). The phenyl ring containing ipso carbon C(37) is nearly perpendicular to and bisects the pyrrole ring containing N(4). The N(4)−Co−Sn−C(37) torsional angle is 3.2° and the plane of the phenyl ring is inclined 82° to the pyrrole ring plane. The other two phenyl rings are inclined at angles of 26 and 17° to the porphyrin plane. Given the asymmetry of the arrangement of the phenyl rings, the irregularity of the N−Co−Sn and C−Sn−C angles and the 11.3° inclination of the plane of the ipso carbons to the porphyrin plane are not suprising. At first glance, the arrangement of the $SnPh_3$ group might suggest an intramolecular interaction between the π systems of the two phenyl rings and the porphyrin. However, an examination of the packing, Figure 2, reveals that the arrangement allows for a 3.2 Å edge-to-face, π-type interaction between H(41A) of one molecule and C(44) and C(45) of an inversion-related $(1 - x, 1 - y, -z)$ molecule. Interactions of this type are common and can be observed in the structure of $SnPh_4$.[41] Whatever its origin may be, the asymmetric arrangement of the $SnPh_3$ group does not persist in solution on the NMR time scale.

Reactivity of Co^{III}(OEP)$SnPh_3$. Co^{III}(OEP)$SnPh_3$ is soluble and stable in many solvents including various aromatics and halomethanes. Pyridine binds reversibly to afford the six-coordinate complex Co^{III}(OEP)($SnPh_3$)(C_5H_5N). Titration of a benzene solution of Co^{III}(OEP)$SnPh_3$ with pyridine resulted in changes in the UV−vis spectrum. Isosbestic points were observed at 440 and 497 nm. Prominent shoulders at 407 and 518 nm decreased and a new band appeared at 466 nm. In addition, the ^1H chemical shifts of the complex in C_5D_5N increased by 0.1 to 0.3 ppm relative to other solvents and the difference between the shifts of the diastereotopic ethyl CH_2 protons increased to 0.134 ppm from that of a previously unresolved multiplet. Neither acetonitrile nor DMF appears to coordinate to Co^{III}(OEP)$SnPh_3$.

The thermal stability of solutions of Co^{III}(OEP)$SnPh_3$, both anaerobic and aerobic, is truly remarkable. Anaerobic solutions were stable indefinitely in all solvents at room temperature. Aerobic solutions in freshly purified dichloromethane and chloroform were stable for more than 24 h. Aerobic solutions in toluene showed barely detectable (<3%) decomposition to Co^{II}(OEP) after 12 h at 75 °C. Similarly, little decomposition to Co^{II}(OEP) was observed after 12 h when an anerobic solution in benzene was heated at 120 °C in a sealed pressure vessel. Decomposition products resulting from the $SnPh_3$ group were not detected by NMR in the latter two experiments.

Although Co^{III}(OEP)$SnPh_3$ is inert to O_2 in solution, electrochemical oxidation of the complex is facile. Cyclic voltammetry showed a completely irreversible oxidation process with an anodic peak at +0.31 V relative to Ag/Ag^+. Continued sweeping of the potential past this process revealed two reversible one-electron oxidations at potentials comparable to those of Co^{II}(OEP), which suggests that this complex is a product of the irreversible oxidation. The peak height of the irreversible oxidation process was somewhat larger than that of the one-electron processes. As expected from this result, addition of excess I_2 (2 equiv) to a benzene solution of Co^{III}(OEP)$SnPh_3$ resulted in an immediate color change and afforded Co^{III}(OEP)I and Ph_3SnI, eq 5.

$$Co^{III}(OEP)SnPh_3 + I_2 \rightarrow Co^{III}(OEP)I + Ph_3SnI \qquad (5)$$

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The Co−Sn bond was also cleaved, albeit slowly, by photochemical activation. Exposure of a chloroform solution of $Co^{III}(OEP)SnPh_3$ to Pyrex-filtered UV light led, over the course of 24 h, to complete conversion to Ph_3SnCl and a mixture of $Co^{II}(OEP)$ and $Co^{III}(OEP)Cl$. Photolysis in benzene or toluene afforded $Co^{II}(OEP)$ as the sole detectable decomposition product. Decomposition was only about 50% complete after 3 days irradiation in anaerobic solutions. Similar conversions were achieved after 12 h irradiation of aerobic solutions.

Attempts to cleave the Co−Sn bond reductively were unsuccessful. $Co^{III}(OEP)SnPh_3$ did not react with excess $NaBH_4$ in benzene/methanol solution. The complex was also inert toward H_2. No reaction was detected after 5 days at room temperature under 1 atm of H_2 or even after 12 h at 120 °C under 60 psi of H_2 in a sealed pressure vessel. Photolysis of solutions at both of these H_2 pressures led to formation of some $Co^{II}(OEP)$ but no formation of Ph_3SnH.

We investigated the transfer of the Ph_3Sn group from $Co^{III}(OEP)SnPh_3$ to a second cobalt porphyrin, eq 6. Anerobic

$$Co^{III}(OEP)SnPh_3 + Co^{II}(TTP) \rightarrow Co^{II}(OEP) + Co^{III}(TTP)SnPh_3 \quad (6)$$

solutions containing 1 equiv of $Co^{III}(OEP)SnPh_3$ and 1.5 equiv of $Co^{II}(TTP)$ were prepared in benzene and toluene and heated or photolyzed under various conditions. Thermally initiated transfer was not observed at temperatures below 120 °C. Observation of the center lines of the *ortho*-phenyl multiplet of $Co^{III}(TTP)SnPh_3$ at 5.17 ppm established that a small amount of transfer occurred after 12 h at this temperature. Transfer was only about 50% complete after 48 h at 120 °C. Photolysis also effected the transfer reaction, which took about 3 to 4 days to reach completion.

Investigations of $Co^{III}(OEP)CX_3$ Complexes (X = Cl, Br, I). Over the course of several hours, reaction of $Co^{II}(OEP)$ with 1 equiv of $CBrCl_3$ in benzene resulted in the appearance of a new singlet at 10.68 ppm and a CH_3 triplet and CH_2 multiplet characteristic of a five-coordinate, diamagnetic $Co^{III}OEP$ complex. Larger excesses of $CBrCl_3$ increased the speed of the reaction (min vs h) but also led to the appearance of new peak at 10.82 ppm and an increase in the complexity of the CH_2 multiplet. Analogous changes were observed in chloroform solution. The new singlet appeared at 10.51 ppm. Subsequently, singlets appeared at 10.65 ppm and then at 9.95 ppm. The growth of each of the latter two singlets came at the expense of the singlet(s) that appeared earlier. Conversion to the latter two singlets was increased by larger excess of $CBrCl_3$.

NMR data were not available in the literature for $Co^{III}(OEP)Br$ or $Co^{III}(OEP)Cl$ in either solvent. Authentic samples of $Co^{III}(OEP)X$ (X = Cl, Br, I) were prepared to aid in idenification of the species whose formation is described above and subsequently. The ^1H chemical shift data for these complexes are presented in Table 3, which also includes data for the $Co^{III}(OEP)CH_mX_n$ ($m + n = 3$) complexes described in this section. The chemical shifts of these complexes are markedly dependent on the solvent. The 0.86 ppm increase in the shift in of the $Co^{III}(OEP)Cl$ *meso*-protons on going from chloroform to benzene is particularly noteworthy and unexpected. The large shift difference between the diastereotopic CH_2 protons of $Co^{III}(OEP)X$, the smaller shift differences for the protons in $Co^{III}(OEP)CH_mX_n$, and the dependence of the shift differences on X are also noteworthy.

On the basis of the data obtained, we identified the previously unknown complex $Co^{III}(OEP)CCl_3$ as the initial product of the reaction of $Co^{II}(OEP)$ with $CBrCl_3$. At extended reaction times, $Co^{III}(OEP)Br$ and finally $Co^{III}(OEP)Cl$ are produced.

Table 3. ^1H NMR Data for $Co^{III}(OEP)X$ and $Co^{III}(OEP)CH_nX_{3-n}$ Complexes (X = Cl, Br, I; $n = 0-2$)[a]

axial ligand	solvent	*meso*-C**H**[b]	C**H**$_2$[c]	Δ*δ*C**H**$_2$	C**H**$_3$[d]	C**H**$_n$X$_{3-n}$[e]
Cl	C_6D_6	10.83	3.93	0.25	1.81	
	$CDCl_3$	9.97	4.15	0.49	1.89	
Br	C_6D_6	10.82	3.89	0.16	1.79	
	$CDCl_3$	10.65	4.06	0.20	1.88	
I	C_6D_6	10.52	3.91	0.13	1.82	
	$CDCl_3$	10.42	4.08	0.14	1.90	
CCl_3	C_6D_6	10.68	3.96	0.12	1.83	
CBr_3	C_6D_6	10.74	3.97	*f*	1.80	
CI_3	C_6D_6	10.89				
$CHCl_2$	C_6D_6	10.41	3.93	0.06	1.83	−0.95
$CHBr_2$	C_6D_6	10.40	3.93	0.05	1.83	−1.20
CH_2Br	C_6D_6	10.32				−2.06
CHI_2	C_6D_6	10.38	3.92	*f*	1.83	−2.29
CH_2I	C_6D_6	10.31				−2.69

[a] ppm relative to TMS at 21 °C. [b] Singlet, 4 H. [c] Multiplet, 16 H. [d] Triplet, 24 H. [e] Singlet, *n* H. [f] Diastereotopic protons not resolved.

We attempted to prepare $Co^{III}(OEP)CCl_3$ by other routes in order to confirm this assignment. $Co^{II}(OEP)$ did not react with excess CCl_4. However, $Co^{I}(OEP)^-$ reacted with either $CBrCl_3$ or CCl_4 in THF solution, eq 7, where X = Br or Cl, to afford

$$Na[Co^{I}(OEP)] + XCCl_3 \rightarrow NaX + Co^{III}(OEP)CCl_3 \quad (7)$$

a complex whose ^1H NMR spectrum in benzene was identical with the putative $Co^{III}(OEP)CCl_3$ obtained above. The Co(I) reactions also produced a barely detectable amount of a product that had a *meso*-proton singlet at 10.41 ppm and a high field singlet at −0.95 ppm. This product was identified as $Co^{III}(OEP)CHCl_2$ and was prepared independently by reaction of $Co^{I}(OEP)^-$ with $CHCl_3$. Thus, exchange between the halogen of the trihalomethyl species and a hydrogen pool (THF) occurs during the course of the Co(I) reactions.

$Co^{III}(OEP)CCl_3$ is not stable in solution. It decomposes to $Co^{III}(OEP)Cl$ over the course of several hours. Decomposition is immediate if the solution is exposed to air. The complex did not survive attempts at chromatographic purification or recrystallization. In contrast, $Co^{III}(OEP)CHCl_2$ is reasonably air stable in solution.

The investigation of trihalomethyl complexes was extended to include CBr_3 and CI_3 complexes. $Co^{I}(OEP)^-$ reacted with CBr_4 to afford roughly equal amounts of $Co^{III}(OEP)CBr_3$ and $Co^{III}(OEP)CHBr_2$. The latter complex was prepared independently by reaction of $Co^{I}(OEP)^-$ with $CHBr_3$, a reaction that also generated a small amount of $Co^{II}(OEP)CH_2Br$. $Co^{III}(OEP)CBr_3$ was also produced by the reaction of $Co^{II}(OEP)$ with excess CBr_4. At longer reaction times the complex decomposed to afford $Co^{III}(OEP)Br$. Iodomethyl containing species were much less stable. Reaction of $Co^{I}(OEP)^-$ with CI_4 afforded only $Co^{III}(OEP)CHI_2$ and small amounts of $Co^{III}(OEP)CH_2I$, both of which were also obtained by reaction of $Co^{I}(OEP)^-$ with CHI_3. Reaction of $Co^{II}(OEP)$ with 2 equiv of CI_4 in benzene led to rapid formation (10 min) of a diamagnetic species with a *meso*-proton singlet at 10.89 ppm, which appears be $Co^{III}(OEP)CI_3$. However, in less than 1 h, an additional singlet appeared at 10.79 ppm, and several broad peaks appeared in the baseline. Overnight, the broad peaks became the dominant features in the spectrum. The analogous reaction in chloroform solution afforded a mixture that contained mostly $Co^{III}(OEP)I$ and minor amounts of four species. The minor species, whose *meso*-proton singlets do not correspond to those of any identified complex examined herein, disappeared as the reaction progressed.

Discussion

Metalloporphyrin complexes containing heteronuclear metal−metal bonds have been of interest for some time.[42] However, relatively few examples exist that involve a metal−metal bond between the group IV metal tin and a transition metal. The only porphyrin complex previously known to have a Co−Sn bond was the tin porphyrin, (TPP)Sn−Co(CO)$_3$−Hg−Co(CO)$_4$.[43] Iron(III) and rhodium(III) porphyrin complexes with tin-containing donor groups as axial ligands have been reported,[20,44,45] but only Rh^{III}(TTP)SnCl$_3$ was characterized by X-ray diffraction.[45] Thus, Co^{III}(OEP)SnPh$_3$ is of interest with respect to both its previously unknown composition type and the structural and reactivity information that it provides.

The formation of Co^{III}(OEP)SnR$_3$ by reaction of trialkylstannanes with Co^{III}(OEP)CH$_3$ or Co^{II}(OEP), eq 2 and 3, respectively, finds precedent in the reactions of stannanes with organoiron(III) porphyrin and metal−metal bonded, dimeric Rh(II) porphyrin complexes.Tributyltin hydride reacts with propyl or butyl-Fe(p-CH$_3$OTPP) at 25 °C to afford the paramagnetic complex Fe^{III}(p-CH$_3$OTPP)SnBu$_3$ and propane or butane.[44] The reaction proceeds by a metathetical, free-radical mechanism, eqs 8−10, with M = Fe and R′ = Bu. Fe^{III}(p-CH$_3$OTPP)SnBu$_3$ was characterized in situ by NMR but was not isolated. The complex decomposed over a period of hours at 25 °C but decomposed rapidly when exposed to air. The reaction of Ph$_3$SnH with alkyl-Fe^{III}(OEP) or alkyl-Fe^{III}(TTP) lead to reduction to Fe^{II}(P) and formation of hexaphenylditin, eq 11.[46] Formation of hexaphenylditin establishes that Ph$_3$Sn$^\bullet$ radicals recombine, eq 12, rather than being captured by Fe^{II}(P), eq 10. Although the latter result appears to contradict the first, the reaction, which was conducted as part of an investigation to determine the iron−carbon bond dissociation energy, was carried out at 70 °C and at a much lower concentration of iron porphyrin. Decomposition of Fe^{III}(P)SnPh$_3$ would likely be rapid under these conditions. The metal−metal bonded, dimer [Rh^{II}(OEP)]$_2$ reacts with tributyltin hydride or triphenyltin hydride to afford Rh^{III}(OEP)SnBu$_3$ or Rh^{III}(OEP)SnPh$_3$, respectively.[20] Both complexes are sufficiently stable to survive chromatography and have ^{1}H chemical shifts that are quite similar to the data reported herein for the corresponding cobalt complexes. Coupling between ^{103}Rh and ^{119}Sn observed in the ^{119}Sn NMR spectrum was offered as evidence of a direct Rh−Sn bond. Formation of the complexes was reported to occur by the reaction in eq 13, based upon a slightly greater than 50% yield of Rh^{III}(OEP)SiR$_3$ observed in reactions of the dimer with some silanes. This might be open to question, though, because H$_2$ was not actually observed, HRh^{III}(OEP) is a stable compound, and the yields with the two stannanes were both slightly less than 50%.

$$\mathrm{R{-}M^{III}(P) \rightleftharpoons R^\bullet + M^{II}(P)} \qquad (8)$$

$$\mathrm{R^\bullet + R'_3SnH \rightarrow RH + R'_3Sn^\bullet} \qquad (9)$$

$$\mathrm{R'_3Sn^\bullet + M^{II}(P) \rightarrow M^{III}(P)SnR'_3} \qquad (10)$$

$$\mathrm{R{-}Fe^{III}(P) + Ph_3SnH \rightarrow Fe^{II}(P) + {}^1/_2Ph_3Sn{-}SnPh_3 + RH} \qquad (11)$$

$$\mathrm{2R'_3Sn^\bullet \rightleftharpoons R'_3Sn{-}SnR'_3} \qquad (12)$$

$$\mathrm{2R'_3SnH + [Rh^{II}(OEP)]_2 \rightarrow 2Rh^{III}(OEP)SnR'_3 + H_2} \qquad (13)$$

Our evidence suggests that the reaction of eq 2 also proceeds by a mechanism consisting of eqs 8−10 (M = Co). The rates of reaction with Bu$_3$SnH and Ph$_3$SnH are the same because homolysis of the cobalt−carbon bond, eq 8, is rate limiting. The presence of Co^{II}(OEP) in impure samples of Co^{III}(OEP)CH$_3$ slows the reaction by accelerating the reverse of eq 8. In other words, Co^{II}(OEP) competes effectively with the stannane for capture of the alkyl free radical. Although the Co−C bond is 10−15 kcal/mol stronger than the Fe−C bond,[46] the formation of the C−H bond in methane is sufficiently exothermic to drive the process. Capture of the stannyl radical by Co^{II}(OEP), eq 10, rather than recombination, eq 12, suggests that the Co−Sn bond is substantially stronger than the Fe−Sn bond.

The reaction of eq 3 was unexpected. H$_2$ formation is dependent upon the presence of both Co^{II}(OEP) and Ph$_3$SnH. Thus, the mechanism probably consists of the reactions in eqs 14, 15, and 10 (M = Co). HCo^{III}(OEP) has been implicated in several reactions[24−29] but is too unstable to accumulate in spectroscopically detectable quantities. Thus, eq 14 was expected to be rather unfavorable. Apparently, the forward rate of eq 14 is sufficiently rapid and the energy released by formation of H$_2$ and a Co−Sn bond is sufficiently large to drive eq 3.

$$\mathrm{Co^{II}(OEP) + R'_3SnH \rightleftharpoons HCo^{III}(OEP) + R'_3Sn^\bullet} \qquad (14)$$

$$\mathrm{2HCo^{III}(OEP) \rightarrow 2Co^{II}(OEP) + H_2} \qquad (15)$$

The failure of eq 3 to reach completion in several days under the conditions investigated (sealed NMR tube) led us to examine whether eq 3 might achieve an equilibrium. Co^{III}(OEP)SnPh$_3$ did not react with H$_2$, even at elevated temperature and pressure. The strong Co−Sn bond, below, disfavors the reverse of eq 10, keeps the concentration of Co^{II}(OEP) low, and strongly inhibits the reverse of eq 15, a termolecular reaction that has been demonstrated for Rh(II) porphyrins.[9,19] Thus, the failure of eq 3 to reach completion under the conditions studied reflects the kinetics of the reaction rather than its position of equilibrium.

The limited extent to which Co^{III}(OEP)SnPh$_3$ decomposed thermally could be the consequence of either a truly high activation energy for Co−Sn bond homolysis (i.e. strong Co−Sn bond) or the persistent radical effect.[47,48] Irreversible destruction of some Ph$_3$Sn$^\bullet$ radical, either through recombination, eq 12, or reaction with a trap like solvent or O$_2$, would lead to a persistent population of the metalloradical Co^{II}(OEP). The persistent metalloradical could trap newly formed Ph$_3$Sn$^\bullet$ and reform Co^{III}(OEP)SnPh$_3$, eq 10, before the radical could undergo the irreversible reactions. To assess the relative

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importance of these effects, experiments were conducted in which a competing, spectroscopically distinguishable cobalt(II) porphyrin was added. Rapid transfer of the Ph_3Sn group to the second cobalt(II) porphyrin relative to decomposition would establish the dominance of the persistent radical effect. This was not observed. Thus, the rate of homolysis of the Co−Sn bond at 120 °C is truly slow. The Co−Sn bond must be substantially stronger than the Co−C bond, which can be estimated to be greater than 30 kcal/mol in the five-coordinate Co^{III}(OEP)R complexes.[30] Consistent with this, Co^{III}(OEP)R complexes react rapidly with O_2, but $Co^{III}(OEP)SnR_3$ complexes are inert. The Ph_3Sn derivatives of cobaloximes are also stable toward O_2 and have good thermal stabilities.[49]

The Co−Sn bond is readily cleaved by oxidation or photolysis with intense light. One-electron oxidation of the metal−metal σ-bonding HOMO decreases the formal bond order from 1 to 0.5. In an analogous situation, the decrease in bond order upon one-electron reduction of Co−C bonded complexes results in a $>10^{15}$ acceleration of the homolysis rate.[50−52] The cyclic voltammograms of several bimetallic indium porphyrin complexes (P)InM(L) exhibit oxidative instability like that of $Co^{III}(OEP)SnPh_3$.[53] The enhanced current of the first, totally irreversible oxidation processes in these systems was attributed to oxidation at the same potential of some of the $M(L)^\bullet$ radical generated by rapid cleavage of the metal−metal bond. In contast to the bond cleavage observed here, oxidation of alkyl- and aryl- Fe(III) and Co(III) porphyrin complexes results in intramolecular migration of the alkyl or aryl group from the metal to nitrogen to afford an N-substituted porphyrin complex.[54−58]

In contrast to the enhanced stability of the Co−Sn bond, the Co−C bond in $Co^{III}(OEP)CX_3$ is notably weaker than the Co−C bond in alkylcobalt(III) porphyrin complexes. Formation of these complexes from Co^{II}(OEP) probably results from homolysis of the C−X bond, eq 16, followed by capture of the resulting

$$CX_4 \rightleftharpoons X^\bullet + X_3C^\bullet \quad (16)$$

$X_3C^\bullet$ radicals, eq 17. The weakening of the C−X bond with

$$Co^{II}(OEP) + X_3C^\bullet \rightleftharpoons Co^{III}(OEP)CX_3 \quad (17)$$

heavier halogens and concomitant stabilization of the $X_3C^\bullet$ radical resulted in successful formation of $Co^{III}(OEP)CX_3$ with $CBrCl_3$, CBr_4, and CI_4 whereas CCl_4 failed to react. It was also responsible for the decreasing stability of $Co^{III}(OEP)CX_3$ complexes with heavier halogens. An alternative mechanism involving halogen atom abstraction from CX_4, eq 18, followed

$$Co^{II}(OEP) + CX_4 \rightleftharpoons Co^{III}(OEP)X + X_3C^\bullet \quad (18)$$

by capture of the resulting $X_3C^\bullet$ radicals, eq 17, has been proposed for the formation of trihalomethylcobaloximes from cobaloximes(II) and tetrahalomethanes.[59] This mechanism does not appear to operate here, given that Co^{III}(OEP)X is not an intial product of the reaction.

The substantial increase in the strength of the Co−Sn bond relative to the Co−C bond is remarkable and unexpected. It suggests that other cobalt(III) porphyrin complexes containing heteronuclear metal−metal bonds might have sufficient stability to be synthesized and isolated. It also raises the questions of whether the $Co^{III}(OEP)ER_3$ complexes with the lighter group IV elements Si and Ge are thermodynamically and kinetically stabile and how that stability varies with E. Future work in our laboratory will pursue these issues.

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Supporting Information Available: An X-ray crystallographic file, in CIF format, is available on the Internet only. Access information is given on any current masthead page.

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