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Synthesis and Characterization of Stable Tin Porphyrins with a Carbon σ-Bonded Axial Ligand

K. M. Kadish,*[1a] D. Dubois,[1a] S. Koeller,[1b] J.-M. Barbe,[1b] and R. Guilard*[1b]

Department of Chemistry, University of Houston, Houston, Texas 77204-5641, and Laboratoire de Synthèse et d'Electrosynthèse Organométalliques, associé au CNRS (URA 33), Faculté des Sciences "Gabriel", 6 Boulevard Gabriel, 21100 Dijon, France

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The synthesis and isolation of tin porphyrins with a metal–carbon bond is described. The investigated compounds are represented as (P)Sn(CH$_3$)I, where P is the dianion of octaethylporphyrin (OEP), tetra-*p*-tolylporphyrin (TpTP), tetra-*m*-tolylporphyrin (TmTP), or tetramesitylporphyrin (TMP). The (P)Sn(CH$_3$)I complexes were prepared by reacting (P)Sn^{II} with methyl iodide in THF. The σ-bonded complexes were characterized by ^{1}H NMR, IR, and UV–visible spectroscopy as well as by electrochemistry, all of which give data consistent with a single metal–carbon covalent bond. Electrochemistry was also used to monitor the in situ formation of the σ-bonded products.

Introduction

The synthesis and characterization of numerous main group metalloporphyrins containing either one or two metal–carbon σ-bonded axial ligands have been described in the literature.[2,3] These organometallic compounds are represented as (P)M(R), (P)M(R)(X), or (P)M(R)$_2$, where P is the dianion of a given porphyrin, R is an alkyl or aryl axial ligand, and M is a group 13 or group 14 metal ion in the +3 or +4 oxidation state.

The reactivity and physicochemical properties of (P)M(R), where M = Al, Ga, In, or Tl, are known under a variety of solution conditions,[2-4] and a great deal of information is also available for (P)M(R)$_2$, where M = Si[5] or Ge.[6-15] However, far less data are available for σ-bonded Sn porphyrins, due in large part to the fact that they are photoactive, O$_2$ sensitive, and readily decompose into the tin(IV) peroxo or dihydroxo derivatives.[8] The existence of (P)Sn(R)$_2$ and (P)Sn(R)X (X$^-$ = Br$^-$, Cl$^-$, R = Et, Pr, Bu, Me$_3$SiCH$_2$) has been claimed in the literature,[8,11,12] but these complexes have never been isolated in the solid state.

Germanium σ-bonded[16] and tin dihalide[17] metalloporphyrins play a significant role in anticancer drug action, and it is anticipated that tin–carbon σ-bonded porphyrins should also exhibit activity toward neoplastic tissues. Moreover, parallel studies in biology have described tin porphyrins as inhibitors of bilirubin synthesis and it has been postulated that a tin protoporphyrin can replace modified heme before lysis by heme oxygenase.[18-20] Thus, the availability of stable σ-bonded Sn(IV) porphyrins should be of interest in studying some biological systems.

The synthesis of stable tin(IV)–carbon σ-bonded porphyrins is now demonstrated for the first time in the present paper. These compounds, represented as (P)Sn(CH$_3$)I, where P is the dianion of octaethylporphyrin (OEP), tetra-*p*-tolylporphyrin (TpTP), tetra-*m*-tolylporphyrin, (TmTP) or tetramesitylporphyrin (TMP), were characterized by UV–visible, IR, and ^{1}H NMR spectroscopy as well as by electrochemistry.

Experimental Section

Chemicals. The synthesis and handling of each porphyrin was carried out under an argon atmosphere. All common solvents were thoroughly dried in an appropriate manner and were distilled under argon prior to use. All operations were carried out using Schlenk techniques and dry oxygen-free solvents. The glassware was heated under vacuum for 2 h at 250 °C before use. Tetrabutylammonium hexafluorophosphate, TBA(PF$_6$), was purchased from Fluka Co., twice recrystallized from ethyl acetate, and dried in a vacuum oven at 40 °C prior to use.

(P)Sn complexes where P = OEP, TpTP, TmTP, or TMP were synthesized by metalation of the corresponding (P)H$_2$ free base porphyrin with anhydrous SnCl$_2$ using literature procedures.[21]

(OEP)Sn(CH$_3$)I. Methyl iodide (16 mmol) was added to a solution of (OEP)Sn (0.31 mmol) in 50 mL of THF at room temperature to give (OEP)Sn(CH$_3$)I, which immediately precipitated. Further purification of (OEP)Sn(CH$_3$)I was not possible due to the low stability of this complex. Yield: 80%. Anal. Calcd for C$_{37}$H$_{47}$N$_4$ISn: C, 56.08; H, 5.97; N, 7.06. Found: C, 56.24; H, 5.78; N, 6.97. IR (CsI): 530 (Sn–C) cm^{-1}. UV–visible: 361, 409 (Soret band), 541, 578 nm. ^{1}H NMR (CDCl$_3$) (δ, ppm): 10.73 (s, 4 H, *meso*-H), 4.35 (m, 16 H, α-CH$_2$), 2.04 (t, 24 H, β-CH$_3$), –5.00 (s, 3 H, $J_{\text{Sn-H}}$ = 88 Hz, Sn–CH$_3$).

(TpTP)Sn(CH$_3$)I. This compound was prepared using the same procedure as for the OEP analogue. The reaction required 5–10 h for completion, and (TpTP)Sn(CH$_3$)I was soluble in THF. Yield: 40%. It was recrystallized from toluene. Anal. Calcd for C$_{49}$H$_{39}$N$_4$ISn: C, 63.32; H, 4.23; N, 6.03. Found: C, 63.53; H, 4.16; N, 6.24. IR (CsI): 520 (Sn–C) cm^{-1}. UV–visible: 347, 438 (Soret band), 578, 624 nm. ^{1}H NMR (C$_6$D$_6$) (δ, ppm): 9.12 (s, 8 H, pyr H), 8.08 (d, 4 H, *o*-H), 7.95

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(d, 4 H, o′-H), 7.25 (d, 4 H, m-H), 7.20 (d, 4 H, m′-H), 2.39 (s, 12 H, p-CH_3), –5.56 (s, 3 H, J_{Sn-H} = 83 Hz, Sn–CH_3).

(TmTP)Sn(CH_3)I. (TmTP)Sn(CH_3)I was obtained as described for (TpTP)Sn(CH_3)I. Yield: 46%. It was recrystallized from toluene/heptane (1/1). Anal. Calcd for $C_{49}H_{39}N_4ISn$: C, 63.32; H, 4.23; N, 6.03. Found: C, 64.64; H, 4.77; N, 5.18. IR (CsI): 523 (Sn–C) cm^{-1}. UV–visible: 347, 431 (Soret band), 579, 636 nm. ^1H NMR (C_6D_6) (δ, ppm): 9.08 (m, 8 H, pyr H), 8.01 (m, 8 H, phenyl H), 7.33 (m, 8 H, phenyl H), 2.28 (m, 12 H, m-CH_3), –5.52 (s, 3 H, J_{Sn-H} = 83 Hz, Sn–CH_3).

(TMP)Sn(CH_3)I. The same procedure as above was used to prepare this compound. Yield: 50%. It was recrystallized from toluene. Anal. Calcd for $C_{57}H_{55}N_4ISn$, C_7H_8: C, 67.20; H, 5.60; N, 4.94. Found: C, 68.21; H, 5.63; N, 4.94. IR (CsI): 520 (Sn–C) cm^{-1}. UV–visible: 340, 431 (Soret band), 590, 636 nm. ^1H NMR (C_6D_6) (δ, ppm): 8.93 (s, 8 H, pyr H), 7.13 (s, 4 H, m-H), 7.00 (s, 4 H, m′-H), 2.40 (s, 12 H, p-CH_3), 2.03 (s, 12 H, o-CH_3), 1.76 (s, 12 H, o′-CH_3), –5.17 (s, 3 H, J_{Sn-H} = 83 Hz, Sn–CH_3).

Physicochemical Measurements. Mass spectra were obtained in the positive FAB mode on a Kratos Concept IS mass spectrometer equipped with a Sun 3/80 data system. Xenon was used as a primary atom beam at 8 kV and 1 μA. 3-Nitrobenzyl alcohol was the matrix. ^1H NMR spectra were recorded at 400 MHz on a Bruker WM 400 spectrometer of the "Centre de Spectrométrie Moléculaire de l'Université de Bourgogne". These spectra were measured in C_6D_6 or $CDCl_3$ ((OEP)Sn(CH_3)I) using tetramethylsilane as internal reference. Infrared spectra were obtained on a Perkin-Elmer 580 B spectrometer. Solid samples were prepared as 1% dispersions in a CsI pellet. Electronic absorption spectra were recorded on a Varian Cary I spectrophotometer. All of the UV–visible spectra were measured in toluene except for (OEP)Sn(CH_3)I, which was spectroscopically characterized in CH_2Cl_2.

Cyclic voltammograms were obtained with the use of a three-electrode system using a platinum button working electrode and a platinum wire counter electrode. A saturated calomel electrode (SCE) served as the reference electrode and was separated from the bulk of the solution by a fritted-glass bridge. A BAS 100 electrochemical analyzer or an IBM EC 225 voltammetric analyzer was used to measure the current–voltage curves. All electrochemical measurements were carried out in a Vacuum Atmospheres Co. glovebox.

Results and Discussion

Synthesis. Two general methods are most often utilized for the synthesis of σ-bonded metalloporphyrins.[2,3] The first involves a reaction of (P)MCl or (P)MCl_2 with a Grignard reagent, while the second involves oxidative addition of an alkyl or aryl halide to a porphyrin with a low-valent central metal. Early attempts to alkylate tin tetraphenylporphyrins, tetraphenylchlorins, or tetraphenylisobacteriochlorins by a Grignard reagent showed that the key intermediate was invariably a $[(P)SnCl_2]^{\bullet-}$ radical anion as shown in eq 1.[11] The expected (P)Sn$(R)_2$ or (P)Sn(R)X complexes were apparently formed, but none of these species were isolated, and they were only characterized in situ by ^1H NMR.

$$(P)SnCl_2 + RMgX \rightarrow [(P)SnCl_2]^{\bullet-} + R^{\bullet} + MgX^+ \quad (1)$$

Oxidative addition has never been utilized for the synthesis of σ-bonded metalloporphyrins with a main group central metal since stable low-valent forms of these compounds generally do not exist. However, the synthesis of four-coordinate tin(II) porphyrins[21] and the facile conversion of Sn(II) to Sn(IV)[22] suggested the use of these low oxidation state complexes as starting materials in the synthesis of σ-bonded Sn(IV) porphyrins. As will be shown, this reaction quantitatively produces monomethyl (P)Sn^{IV}(CH_3)I complexes according to eq 2.

$$(P)Sn^{II} + CH_3I \rightarrow (P)Sn^{IV}(CH_3)I \quad (2)$$

The iodide axial ligand is only weakly bonded to the Sn(IV) metal, and as discussed in later sections, a dissociation occurs to give $[(P)Sn(CH_3)S]^+$ (S = solvent molecule) in the utilized electrochemical solvents. A dissociated Sn(IV) complex is also present in the FAB mass spectrum, which shows $[(P)Sn(CH_3)(m)]^+$ as the major ion where m is the 3-nitrobenzyl alcohol matrix.

Spectroscopic Characterization. UV–visible, ^1H NMR, and IR characteristics of the isolated Sn(IV) porphyrins are given in the Experimental Section. The methylenic protons of (OEP)Sn(CH_3)I are anisochronous, and this is explained by the anisotropy induced by the two different axial ligands. Resonances of the phenyl ring protons of (TpTP)Sn(CH_3)I can also be explained by taking account of this anisotropy. Two signals are attributable to o-H and o′-H sites and resonances of the m-H and m′-H protons appear as two doublets. The (TMP)Sn(CH_3)I derivative has the same behavior and the meta protons give two different signals in the ^1H NMR spectrum. The same pattern occurs for the o-CH_3 groups. All porphyrin proton resonances of the TmTP complex appear as multiplets. The methylic axial ligand proton signal is located between –5.0 and –5.6 ppm, and the shielding is large, as expected for an alkyl group σ-bonded to a main group metal of a metalloporphyrin.[2,3] A coupling is observed between the axial methyl protons and the ^{117}Sn and ^{119}Sn isotopes (see Experimental Section).

The UV–visible spectra of (P)Sn(CH_3)I are similar to spectra reported for (P)Si(R)(OH)[5] and (P)Ge(R)X,[15] where R is an alkyl or aryl group and X is Cl^- or ClO_4^-. The Soret band maximum is located at 409 nm for (OEP)Sn(CH_3)I and varies between 431 and 438 nm for the three investigated tetraaryl derivatives. A characteristic tin–methyl vibration is located at 530 cm^{-1} for (OEP)Sn(CH_3)I, and this peak is located between 520 and 523 cm^{-1} for compounds in the tetraarylporphyrin series. As might be expected, all of these data are similar with values reported for the analogous Si and Ge complexes.[5,15]

Electrochemistry. Cyclic voltammetry was used to characterize the isolated complexes as well as to monitor the in situ conversion of (P)Sn to (P)Sn(CH_3)I in THF. Parts a and b of Figure 1 show cyclic voltammograms of (OEP)Sn^{II} in THF before and after addition of methyl iodide to the solution. Figure 1c shows a cyclic voltammogram of previously isolated (OEP)Sn(CH_3)I under the same solution conditions. As seen in this figure, the addition of CH_3I to a THF solution of (OEP)Sn results in a disappearance of reductions at $E_{1/2}$ = –1.28 and –1.73 V and the appearance of new reductions at –0.70, –1.24, and ≈–1.48 V. The first two half-wave potentials are similar to those observed for previously isolated (OEP)Sn(CH_3)I (Figure 1c). The third reduction in Figure 1b does not appear for the isolated (OEP)Sn(CH_3)I sample and may be due to a (OEP)Sn$(CH_3)_2$ side product formed during the oxidative addition or by reaction of the electroreduced methylated complex with excess methyl iodide which is present in solution. A single reduction has been reported at the same potential for (OEP)Ge$(CH_3)_2$ in PhCN,[15] and this lends support to the proposed (OEP)Sn$(CH_3)_2$ assignment.

Similar electrode reactions occur for all of the investigated porphyrins, and half-wave potentials for the four complexes are summarized in Table I. The first reduction occurs between –0.45 and –0.85 V, while the second is located between –1.02 to –1.29 V, depending on the specific solvent conditions and the porphyrin ring basicity. The values of $E_{1/2}$ are almost identical for samples which had previously been isolated and those which were generated in situ.

The in situ conversion of (OEP)Sn to (OEP)Sn(CH_3)I occurs via the oxidative addition reaction shown in eq 2 and is completed in 2–3 min. A similar reaction is observed with the other (P)Sn^{II} complexes, but 15–20 min are required to generate the final cyclic voltammogram of the σ-bonded species. The generation of

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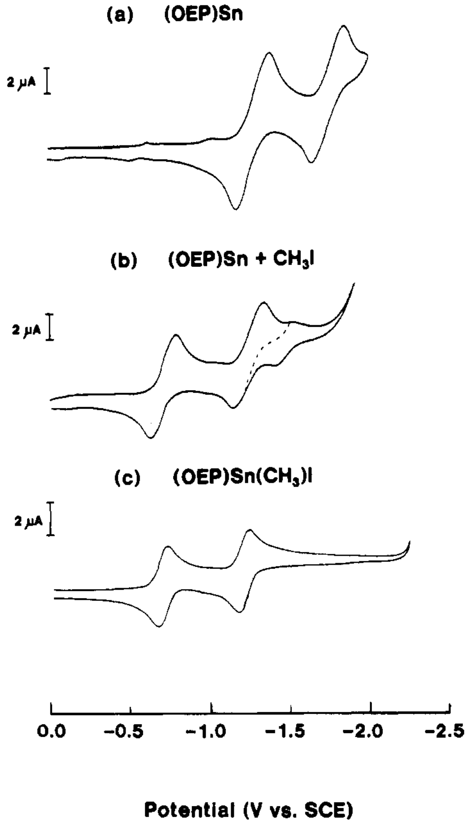

Figure 1. Cyclic voltammograms for the reduction of (a) (OEP)Sn^{II}, (b) (OEP)Sn^{II} plus excess CH_3I, and (c) isolated (OEP)Sn(CH_3)I in THF, 0.1 M TBA(PF_6). Scan rate = 0.1 V/s.

(P)Sn(CH_3)I (P = TpTP, TmTP, TMP) appears to be quantitative in that only two reductions are seen under all solution conditions. Both reductions are reversible and involve the stepwise addition of two electrons, as shown in eq 3, where S = PhCN or THF.

$$[(P)Sn(CH_3)S]^+ \overset{+e^-}{\rightleftharpoons} [(P)Sn(CH_3)S]^\bullet \overset{+e^-}{\rightleftharpoons} [(P)Sn(CH_3)S]^- \quad (3)$$

The electroactive complex in eq 3 is formulated as $[(P)Sn(CH_3)S]^+$, rather than as associated (P)Sn(CH_3)I, where S = THF or PhCN. Solvent molecules are known to bind to Sn(IV) metalloporphyrins with anionic axial ligands[22,23] and, in so doing, form $[(P)Sn(X)S]^+$, where X is a halide or pseudohalide ion and S a solvent molecule such as py, THF, or PhCN.

Table I. Half-Wave Potentials (V vs SCE) for Reduction of (P)Sn(CH_3)I in PhCN and THF, 0.1 M TBA(PF_6)

		$E_{1/2}$ (V vs SCE)	
porphyrin ring, P	solvent	1st redn	2nd redn
TpTP	PhCN	−0.64	−1.06
	THF	−0.50	−1.04
TmTP	PhCN	−0.62	−1.04
	THF	−0.45	−1.02
TMP	PhCN	−0.62	−1.10
	THF	−0.49	−1.15
OEP	PhCN	−0.85	−1.29
	THF	−0.71	−1.21

Undissociated $(P)Sn(X)_2$ complexes[23] are more difficult to reduce than the $[(P)Sn(X)S]^+$ species as evidenced by the fact that the one-electron, ring-centered reduction of $[(P)Sn(ClO_4)S]^+$ or $[(P)Sn(PF_6)S]^+$ (S = py, THF, PhCN)[22] occurs at potentials 300–400 mV positive of potentials for undissociated $(P)Sn(OH)_2$ or $(P)Sn(F)_2$.[23] The latter values are similar to potential differences between $E_{1/2}$ for the first reduction of undissociated $(P)Sn(X)_2$ and (P)Sn(CH_3)I under the same solution conditions. These results are all consistent with a single positive charge on the σ-bonded complex. Additional evidence for $[(P)Sn(CH_3)S]^+$, rather than (P)Sn(CH_3)I, in THF and PhCN comes from the large (up to 140 mV) solvent dependence on $E_{1/2}$, as well as from the fact that two oxidations due to free I^- are observed in solutions of genuine (P)Sn(CH_3)I. Finally, as earlier noted, a dissociated Sn(IV) complex is also present in the FAB mass spectrum, which lends further support to the replacement of the iodide of (P)Sn(CH_3)I by a solvent molecule in solution.

In summary, the synthesis of (P)Sn(CH_3)I is straightforward and proceeds via a quantitative oxidative addition reaction involving (P)Sn and CH_3I. (P)Sn(R)X complexes with other σ-bonded groups and anionic ligands should also be obtainable and attempts to generate and isolate such compounds are now underway.

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