Syntheses and Characterizations of Alkyl- and Amidotin Porphyrin Complexes: Molecular Structure of *trans*-Bis(phenylacetylido)(*meso*-tetra-*p*-tolylporphyrinato)tin(IV)

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Treatment of (TTP)$SnCl_2$ (TTP = *meso*-tetra-*p*-tolylporphyrinato dianion) with an excess of lithium amides (LiNHPh, $LiNPh_2$, *o*-$C_6H_4(NHLi)_2$) affords the metathesis products (TTP)$Sn(NHPh)_2$ (**1**), (TTP)$Sn(NPh_2)_2$ (**2**), and (TTP)Sn(*o*-$C_6H_4(NH)_2$) (**3**). Ligand exchanges of **1** with *p*-toluidine and 2,3,5,6-tetrafluoroaniline afford the complexes (TTP)Sn(*p*-$NHC_6H_4Me)_2$ (**4**) and (TTP)$Sn(NHC_6F_4H)_2$ (**5**), respectively. Treatment of (TTP)$SnCl_2$ with the bulky lithium (2,4,6-tri-*tert*-butylphenyl)amide or with PhNLiNLiPh does not form the corresponding amido or azobenzene complexes but produces the reduced product (TTP)Sn. In addition, the reaction of (TTP)-$Sn(NHPh)_2$ with PhHN−NHPh results in the production of (TTP)Sn, azobenzene, and aniline. The diethyl complex (TTP)$SnEt_2$ (**6**) can be prepared via the reaction of (TTP)$SnCl_2$ with 1 equiv of $ZnEt_2$. The dineopentyl complex (TTP)$Sn(CH_2CMe_3)_2$ (**7**) can be detected in the reaction of (TTP)$SnCl_2$ with neopentyllithium. The methyl derivatives *cis*-(TTP)$SnMe_2$ (**8**) and (TTP)SnMeBr (**9**) can be obtained by the treatment of (TTP)$Li_2(THF)_2$ with 1 equiv of Me_2SnBr_2 at low temperature in toluene and CH_2Cl_2, respectively. Treatment of (TTP)$SnCl_2$ with an excess of alkynyllithium salts (LiC≡CPh, LiC≡$CSiMe_3$) affords the metathesis products (TTP)Sn(C≡$CPh)_2$ (**10**) and (TTP)$Sn(C≡CSiMe_3)_2$ (**11**). Complexes **10** and **11** are inert at ambient temperature and are not photosensitive. Complex **10** reacts stepwise with excess MeOH cleanly to convert to (TTP)Sn(C≡CPh)(OMe) (**12**) and then to (TTP)$Sn(OMe)_2$ (**13**) with increasing reaction time. The lability of the axial ligands in these tin porphyrin complexes correlates inversely with the basicity of the axial group. The crystal structure of **10** (monoclinic, $P2_1/c$, a = 10.9424(2) Å, b = 14.5565(5) Å, c = 16.4968(6) Å, $\alpha = 90°$, $\beta = 100.7930(10)°$, $\gamma = 90°$, R_1 = 3.53%, and wR_2 = 8.90%) was determined from X-ray diffraction data.

Introduction

In tin porphyrin chemistry, many derivatives of general formula Sn(por)L_1L_2 (por = general porphyrin dianion; L_1, L_2 = F, Cl, OR, OH, N_3, etc.) have been synthesized and well characterized.[1−4] However, robust tin metalloporphyrin compounds containing one or two metal−carbon σ-bonded axial ligands are still rare. This is in contrast to the numerous main group metalloporphyrins of the types (por)M(R), (por)M(R)-(X), and (por)$M(R_2)$ (R = alkyl, aryl; M = Al, Ga,[5,6] Si[7] Ge,[8] etc.) that have been synthesized and described in the literature. Dialkyltin porphyrins were first reported by Cloutour et al. by using Grignard reagents as the alkyl ligand sources but could not be isolated due to their photoactivity and O_2 sensitivity.[9] The first porphyrin complexes containing an inert tin−carbon bond were synthesized by Kadish et al. by oxidative addition of MeI to Sn^{II}(por).[10] The only other thermally robust but light sensitive dialkyltin porphyrin complexes of types *cis*- and *trans*-Sn(por)Ph_2 were reported in 1996.[11] The cis complex was prepared by transmetalating Li_2(por)(OEt_2) with $SnPh_2Cl_2$. The trans derivative was produced by the reaction of Sn(por)Cl_2 with Ph_2Mg. The only characterized amidotin porphyrin complex is bis(phenyltetrazolato)tin(IV) tetra-*p*-tolylporphyrinate.[12] To the best of our knowledge, no other alkyl- or amidotin porphyrins have been reported.

Tin porphyrins play an important role in antitumor drug action.[13] Previous studies have shown that tin porphyrins could be used to inhibit bilirubin synthesis[14] and to prevent jaundice, a common illness in neonates.[15] It is anticipated that alkyltin porphyrins should also have similar biological activity. Synthesis of robust tin−carbon σ-bonded porphyrins and amidoporphyrins should be of interest in studying their biological relevance.

In this paper, the synthesis of several bis(amido)tin(IV) porphyrins and a series of tin(IV)−carbon σ-bonded porphyrins

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is demonstrated. Their labilities correlate well with the basicity of the axial ligand anions. The X-ray molecular structure of (TTP)Sn(CCPh)$_2$ (TTP = *meso*-tetra-*p*-tolylporphyrinato dianion) is also reported here.

Experimental Section

General Method. The synthesis and handling of each porphyrin were performed under an inert atmosphere either in a glovebox or by Schlenk techniques, unless otherwise mentioned. THF, hexanes, pentane, OEt_2, C_6D_6, and toluene were dried over purple solutions of Na/benzophenone, degassed with three "freeze−pump−thaw" cycles, and stored in the glovebox after being vacuum-transferred. CH_2Cl_2 was dried with P_2O_5, degassed and also stored in the glovebox after being vacuum-transferred. Literature procedures were used to synthesize (TTP)$SnCl_2$,[1] (TTP)Li_2(THF)$_2$,[16] $LiNPh_2$,[17] $LiCH_2CMe_3$,[18] PhNLiNLiPh (*N*,*N*′-dilithiohydrazobenzene),[19] and LiNHPh.[20] Lithium phenylacetylide and *o*-C_6H_4(NHLi)$_2$ were synthesized by the reactions of phenylacetylene and *o*-diaminobenzene with *n*-butyllithium (1.6 M BuLi in hexane) in Et_2O. Lithium (2,4,6-tri-*tert*-butylphenyl)amide and LiC≡CSi(CH$_3$)$_3$ were similarly prepared via the lithiation of 2,4,6-tri-*tert*-butylaniline and (CH$_3$)$_3$SiC≡CH with BuLi in hexanes, respectively. Other chemicals were reagent grade and were used without further purification.

Elemental analyses were performed in house on a Perkin-Elmer CHNS/O analyzer. ^{1}H NMR spectra were obtained at 300 MHz on a Varian VXR-300 spectrometer, and UV−visible spectra were obtained using a Hewlett-Packard HP 8452A diode-array spectrophotometer. X-ray crystallographic analysis was performed by Siemens, Madison, WI, and MS analysis was performed on a Finnigan TSQ 700 mass spectrometer.

Synthesis of *trans*-(TTP)Sn(NHPh)$_2$ (1). To a stirred solution of (TTP)$SnCl_2$ (0.0708 g, 0.0825 mmol) in 15 mL toluene at −34 °C was added PhNHLi (0.0220 g, 0.222 mmol). The solution was warmed to ambient temperature and its color slowly changed from purple to dark green. The solution was stirred subsequently for 21 h and then filtered. The filtrate was concentrated to 1.5 mL and cooled to −34 °C to deposit dark crystals. (TTP)Sn(NHPh)$_2$ was isolated by filtration, washed with 2 mL of hexanes, and dried in vacuo (0.042 g, 52%). ^{1}H NMR (C_6D_6, ppm): 9.08 (s, 8H, β-H), 8.01 (d, 8H, −C_6H_4Me), 7.27 (d, 8H, −C_6H_4Me), 5.87 (m, 6H, −NH*Ph*), 2.40 (s, 12H, C_6H_4*Me*), 2.34 (m, 4H, −NH*Ph*), −4.37 (s, 2H, −N*H*Ph). UV−vis (toluene): 408, 429 (Soret), 565, 609 nm. Anal. Calcd for (TTP)Sn(NHPh)$_2$·$C_6H_5CH_3$ [$SnC_{67}H_{56}N_6$]: C, 75.64; H, 5.31; N, 7.90. Found: C, 76.49; H, 5.40; N, 8.06. The toluene solvate was observed in the ^{1}H NMR spectrum (2.10 ppm, s, 3H) of the sample submitted for elemental analysis.

Synthesis of *trans*-(TTP)Sn(NPh$_2$)$_2$ (2). The preparation was similar to that of **1**. To a stirred solution of (TTP)$SnCl_2$ (0.0749 g, 0.0873 mmol) in 20 mL of toluene at −34 °C was added $LiNPh_2$ (0.0430 g, 0.245 mmol). The solution was warmed to ambient temperature, stirred 17.5 h, and filtered. The green filtrate was concentrated to 1.5 mL and cooled to −34 °C to form microcrystals. The product (TTP)Sn(NPh$_2$)$_2$ was isolated via filtration, washed with 2 mL of hexanes, and dried in vacuo (0.0280 g, 26%). ^{1}H NMR (C_6D_6, ppm): 8.99 (s, 8H, β-H), 8.08 (d, 8H, −C_6H_4Me), 7.33 (d, 8H, −C_6H_4-Me), 6.15 (t, 4H, *p*-H in NPh$_2$), 6.01 (t, 8H, *m*-H in NPh$_2$), 2.91 (d, 8H, *o*-H in NPh$_2$), 2.44 (s, 12H, −C_6H_4*Me*). UV−vis (toluene): 437 (Soret), 570, and 612 nm. Anal. Calcd for (TTP)Sn(NPh$_2$)$_2$·1.5hexane [$SnC_{81}H_{77}N_6$]: C, 77.63; H, 6.19; N, 6.71. Found: C, 78.56; H, 6.01; N, 6.80. The hexanes solvate (1.5 equiv) was observed in the ^{1}H NMR spectrum (1.25 ppm, m, 12H; 0.88 ppm, t, 9H) of the sample submitted for elemental analysis.

Synthesis of (TTP)Sn(*o*-C_6H_4(NH)$_2$) (3). To a stirred solution of (TTP)$SnCl_2$ (0.0448 g, 0.0522 mmol) in 15 mL of toluene at −34 °C was added solid *o*-C_6H_4(NHLi)$_2$ (0.0075 g, 0.063 mmol). The solution was warmed to ambient temperature and stirred for 17 h. By ^{1}H NMR spectroscopy, it was found that about 31% of (TTP)$SnCl_2$ was not reacted. Another 7.0 mg of C_6H_4(NHLi)$_2$ (0.058 mmol) was added to the solution. The mixture was stirred for additional 7 h and then filtered. The filtrate was concentrated to 1.5 mL and cooled to −34 °C to deposit microcrystals. (TTP)Sn(*o*-C_6H_4(NH)$_2$) was isolated via filtration and dried in vacuo (0.0220 g, 47%). ^{1}H NMR (C_6D_6, ppm): 9.11 (s, 8H, β-H), 8.00 (br s, 4H, −C_6H_4Me), 7.89 (br s, 4H, −C_6H_4-Me), 7.24 (d, 8H, −C_6H_4Me), 5.74 (m, 2H, C_6H_4(NH)$_2$), 4.94 (m, 2H, C_6H_4(NH)$_2$), 2.38 (s, 12H, C_6H_4*Me*), −1.38 (s, 2H, C_6H_4(N*H*)$_2$). UV−vis (toluene): 430 (Soret), 562, 606 nm. MS (NH$_3$/CI, negative): *m*/*z* 893.9 (M$^-$ 893.65).

Reaction of (TTP)$SnCl_2$ with PhNLiNLiPh. To an NMR tube were added 0.0088 g of (TTP)$SnCl_2$ (0.010 mmol) and 0.0032 g of PhNLiNLiPh (0.016 mmol). About 0.8 mL of C_6D_6 was also added to the tube. The ^{1}H NMR spectrum was checked after 2 h. It was found that the reaction was complete and only (TTP)Sn and azobenzene (PhNNPh) were formed after the reaction. ^{1}H NMR of (TTP)Sn (C_6D_6, ppm): 9.19 (s, 8H, β-H), 8.02 (br, 8H, −C_6H_4Me), 7.25 (d, 8H, −C_6H_4-Me), 2.40 (s, 12H, −C_6H_4*Me*), identical with the reported data.[21] ^{1}H NMR of PhNNPh (C_6D_6): 8.01 (d, 4H), 7.0−7.18 (m, 6H), identical with the spectroscopy of an authentic sample.

Reaction of (TTP)$SnCl_2$ with Lithium 2,4,6-tri(*tert*-butyl)-phenylamide. An NMR tube was charged with (TTP)$SnCl_2$ (0.0034 g, 0.004 mmol), lithium (2,4,6-tri-*tert*-butylphenyl)amide (0.0031 g, 0.012 mmol), and about 0.7 mL of C_6D_6. After 2 h, an ^{1}H NMR spectrum indicated that the only new product was Sn(TTP) (87% conversion). Approximately 5% of (TTP)$SnCl_2$ was unreacted.

Reaction of (TTP)Sn(NHPh)$_2$ (1) with *p*-Toluidine. An NMR tube was charged with (TTP)Sn(NHPh)$_2$ (0.0052 g, 0.005 mmol), *p*-toluidine (0.0057 g, 0.05 mmol), and about 0.6 mL of C_6D_6. After 3.4 h, the only new product detected by ^{1}H NMR was (TTP)Sn(*p*-$NHC_6H_4Me)_2$ (**4**). The ratio of (TTP)Sn($NHC_6H_4Me)_2$ to **1** was 7:1. This ratio did not change even when the reaction mixture was heated at 80 °C in an oil bath for about 6 h. $PhNH_2$ was also identified. ^{1}H NMR of (TTP)Sn(*p*-$NHC_6H_4Me)_2$ (**4**) (C_6D_6, ppm): 9.07 (s, 8H, β-H), 8.01 (d, 8H, −C_6H_4Me), 7.29 (d, 8H, −C_6H_4Me), 5.67 (d, 4H, −NHC_6H_4Me), 2.40 (s, 12H, −C_6H_4*Me*), 2.34 (d, 4H, −NHC_6H_4Me), 1.77 (s, 6H, −NHC_6H_4*Me*), −4.37 (s, 2H, −N*H*C_6H_4Me).

Reaction of (TTP)Sn(NHPh)$_2$ (1) with 2,3,5,6-Tetrafluoroaniline. An NMR tube was charged with (TTP)Sn(NHPh)$_2$ (0.0052 g, 0.005 mmol), 2,3,5,6-tetrafluoroaniline (0.0073 g, 0.04 mmol), and about 0.6 mL of C_6D_6. The ^{1}H NMR spectrum indicated that reaction was complete within 11.5 h. The only porphyrin product was (TTP)Sn($NHC_6F_4H)_2$ (**5**). $PhNH_2$ was also identified. Pure complex **5** can be isolated via the reaction of complex **1** with excess 2,3,5,6-tetrafluoroaniline in toluene and recrystallized from a minimum amount of toluene/hexanes at −25 °C. ^{1}H NMR of (TTP)Sn($NHC_6F_4H)_2$ (**5**) (C_6D_6, ppm): 9.15 (s, 8H, β-H), 8.09 (d, 8H, −C_6H_4Me), 7.28 (d, 8H, −C_6H_4Me), 5.20 (m, 2H, −NHC_6F_4H), 2.40 (s, 12H, −C_6H_4*Me*), −4.43 (s, 2H, −N*H*C_6F_4H). UV−vis (toluene): 429 (Soret), 568, 613 nm. MS (NH$_3$/CI, negative): *m*/*z* 1116.1 (M$^-$ 1115.7).

Reaction of (TTP)Sn(NHPh)$_2$ (1) with 2,4,6-Tri-*tert*-butylaniline. An NMR tube was charged with complex **1** (0.0048 g, 0.005 mmol), about 0.6 mL of C_6D_6 and 2,4,6-tri-*tert*-butylaniline (0.0054 g, 0.021 mmol) at ambient temperature. No reaction of **1** with 2,4,6-tri-*tert*-butylaniline was observed via ^{1}H NMR after heating the reaction mixture in an oil bath (80 °C) for 23 h.

Reaction of (TTP)Sn(NHPh)$_2$ (1) with 2,4,6-Trimethylaniline. An NMR tube was charged with complex **1** (0.0028 g, 0.003 mmol), about 0.6 mL of C_6D_6, and 2,4,6-trimethylaniline (6.0 μL, 0.04 mmol) at ambient temperature. After 24 h, no reaction was detected via ^{1}H NMR spectroscopy.

Reaction of (TTP)Sn(NHPh)$_2$ (1) with *o*-C_6H_4(NH$_2$)$_2$. In a glovebox, (TTP)Sn(NHPh)$_2$ (0.0022 g, 0.002 mmol), *o*-C_6H_4(NH$_2$)$_2$

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(0.005 mmol, 23 μL of a 0.2 M solution), and 0.54 mL of C_6D_6 were added to an NMR tube. Monitoring the reaction by ^{1}H NMR showed it to reach completion in 6 h. ^{1}H NMR peaks observed for (TTP)Sn(*o*-$C_6H_4(NH)_2$ (ppm): 9.11 (s, 8H, β-H), 8.00 (br, 4H, C_6H_4Me), 7.89 (br, 4H, $-C_6H_4$Me), 7.24 (d, 8H, $-C_6H_4$Me), 5.74 (m, 2H, $C_6H_4(NH)_2$), 4.94 (m, 2H, C_6H_4Me), 2.38 (s, 12H, CH_3), -1.38 (s, 2H, NH). ^{1}H NMR peaks observed for NH_2Ph (ppm): 7.06 (m, partially obscured by *o*-$C_6H_6(NH_2)_2$, 6.71 (m, 2H), 6.34 (d, 4H), 2.77 (br, NH).

Reaction of (TTP)Sn(NHPh)$_2$ (1) with PhNH−NHPh. In a glovebox, (TTP)Sn(NHPh)$_2$ (0.0028 g, 0.003 mmol), PhNH−NHPh (1.3 mg, 0.007 mmol), and 0.7 mL of C_6D_6 were added to an NMR tube. After 2 h, the reaction was complete as monitored by ^{1}H NMR. New products observed were (TTP)Sn, NH_2Ph, and PhN═NPh. ^{1}H NMR peaks observed for (TTP)Sn (ppm): 9.18 (s, 8H, β-H), 8.03 (m, $-C_6H_4$-Me, partially obscured by PhNNPH), 7.26 (d, 8H, $-C_6H_4$Me), 2.40 (s, 12H, CH_3). ^{1}H NMR peaks observed for NH_2Ph (ppm): 7.06 (m, partially obscured), 6.71 (m, partially obscured), 6.36 (d, 4H, *o*-C_6H_5), 2.79 (br s, NH_2). ^{1}H peaks observed for and PhN═NPh (ppm): 8.00 (m, partially obscured), 7.14 (m, partially obscured), 7.12 (m, partially obscured).

Synthesis of *trans*-(TTP)SnEt$_2$ (6). The following procedure was performed primarily in the dark to avoid the photodecomposition of the product. Solutions were exposed to low-level light for short periods for visual examination. The dichloride complex (TTP)$SnCl_2$ (0.0761 g, 0.089 mmol) was dissolved in 20 mL of toluene, and the solution was cooled to −34 °C. To this cooled and stirred purple solution was added 9.1 μL of $ZnEt_2$ (0.089 mmol). This solution was kept at −34 °C in a freezer in the glovebox. After 15.5 h, the resulting green solution was filtered, and the filtrate was concentrated to 2 mL. The concentrate was layered with 5 mL of hexanes, and the mixture was cooled to −34 °C to form a precipitate. The product (TTP)$SnEt_2$ was isolated by filtration and dried in vacuo (0.025 g, 33%). ^{1}H NMR (C_6D_6, ppm): 9.11 (s, 8H, β-H), 8.12 (d, 8H, $-C_6H_4$Me), 7.26 (d, 8H, $-C_6H_4$Me), 2.40 (s, 12H, $-C_6H_4$Me), −3.58 (t, 6H, $-CH_2CH_3$), −6.23 (q, 4H, $-CH_2CH_3$). Further purification failed due to the decomposition of **6**.

Synthesis of *trans*-(TTP)Sn(CH$_2$CMe$_3$)$_2$ (7). The procedure was also performed primarily in the dark like the preparation of **6.** To a stirred purple solution of (TTP)$SnCl_2$ (0.0096 g, 0.011 mmol) in about 5 mL of toluene at −34 °C was added a solution of $LiCH_2CMe_3$ (0.0018 g, 0.023 mmol) in 2 mL of toluene, which was also cooled to −34 °C. The resulting orange-brown solution was maintained at −34 °C in a freezer for 23.5 h. The solution was then dried, and the residue was analyzed by ^{1}H NMR. It was found that the major product corresponded to the target product (TTP)Sn(CH_2CMe_3)$_2$. Other products (possibly four porphyrin products) were not identified. ^{1}H NMR of **7** (C_6D_6, ppm): 9.12 (s, 8H, β-H), 8.22 (d, 8H, $-C_6H_4$Me), 7.29 (d, 8H, $-C_6H_4$Me), 2.40 (s, 12H, $-C_6H_4$Me), −2.22 (s, 18H, $-CH_2CMe_3$), −6.65 (s, 4H, $-CH_2CMe_3$). Compound **7** was not isolated due to its decomposition.

Reaction of (TTP)SnCl$_2$ with LiMe. An NMR tube charged with (TTP)$SnCl_2$ (0.0087 g, 0.010 mmol) and 0.6 mL of C_6D_6 was cooled to less than 5 °C. A methyllithium solution (about 2 equiv, 1.4 M in Et_2O) was added to the NMR tube wrapped with aluminum foil. The solution was warmed to ambient temperature. After 3 h, ^{1}H NMR was checked to find that one of the major products corresponded to *trans*-(TTP)$SnMe_2$. ^{1}H NMR of *trans*-(TTP)$SnMe_2$ (C_6D_6, ppm): 9.11 (s, 8H, β-H), 8.09 (d, 8H, $-C_6H_4$Me), 7.25 (d, 8H, $-C_6H_4$Me), 2.40 (s, 12H, $-C_6H_4$Me), −6.46 (s, 6H, $-CH_3$). The other products (possibly two porphyrins) were not identified. The signal for *trans*-(TTP)$SnMe_2$ disappeared after several hours in the dark to form unidentified products.

Synthesis of *cis*-(TTP)SnMe$_2$ (8). This experiment was done in the dark. To a stirred solution of (TTP)$Li_2(THF)_2$ (0.0460 g, 0.0556 mmol) in 7 mL of toluene at −25 °C was added 1 mL of a toluene solution of $SnMe_2Br_2$ (0.0175 g, 0.0567 mmol) which had been cooled to −25 °C. The solution was maintained at −25 °C in a freezer for about 22.5 h. The solution was filtered, and the filtrate was taken to dryness under reduced pressure to give *cis*-(TTP)$SnMe_2$ (0.020 g, 44%). Further purification failed due to decomposition at ambient temperature. ^{1}H NMR (C_6D_6, ppm): 9.08 (s, 8H, β-H), 8.14 (br s, 4H, $-C_6H_4$Me), 7.93 (br s, 4H, $-C_6H_4$Me), 7.25 (br s, 8H, $-C_6H_4$Me), 2.38 (s, 12H, $-C_6H_4$Me), −3.83 (s, 6H, $-CH_3$). MS (NH_3/CI, positive): *m*/*z* 817 (M^+ 817.6). UV−vis (toluene): 432 (Soret), 628 nm.

Synthesis of *trans*-(TTP)SnMeBr (9). This procedure was similar to that for the preparation of **8**. To a stirred solution of (TTP)$Li_2(THF)_2$ (0.0361 g, 0.0437 mmol) in 10 mL of CH_2Cl_2 at −34 °C was added a solution of $SnMe_2Br_2$ (0.0127 g, 0.0444 mmol) in 1 mL of CH_2Cl_2 which had also been cooled to −34 °C. The mixture was kept at −34 °C for 23 h. After the solution was filtered at ambient temperature, the filtrate was concentrated to 1.5 mL and layered with 5 mL of Et_2O, and the mixture was cooled to −34 °C to deposit microcrystals. The product *trans*-(TTP)SnMeBr was isolated by filtration, washed with 1 mL of Et_2O, and dried in vacuo (0.0220 g, 57%). ^{1}H NMR (C_6D_6, ppm): 9.14 (s, 8H, β-H), 8.08 (d, 4H, $-C_6H_4$Me), 7.87 (d, 4H, $-C_6H_4$-Me), 7.25 (d, 4H, $-C_6H_4$Me), 7.20 (d, 4H, $-C_6H_4$Me), 2.38 (s, 12H, $-C_6H_4$Me), −5.68 (s, 3H, −Me). UV−vis (CH_2Cl_2): 431 (Soret), 565, 608 nm. MS (NH_3/CI, positive), *m*/*z*: 881.2, $(M - H)^+$; 802.6 $(M - Br)^+$; 867.0 $(M - Me)^+$ (M^+ 882.5). The distribution of MS peaks was similar to the isotope pattern of **9** [$SnC_{49}H_{39}BrN_4$]. Anal. Calcd for (TTP)SnMeBr [$SnC_{49}H_{39}N_4Br$]: C, 66.69; H, 4.45; N, 6.35. Found: C, 65.97; H, 4.06; N, 6.29.

Synthesis of *trans*-(TTP)Sn(C≡CPh)$_2$ (10). To a stirred solution of (TTP)$SnCl_2$ (0.0784 g, 0.0913 mmol) in 20 mL of toluene at −20 °C was added PhC≡CLi (0.0341 g, 0.315 mmol). The resulting solution was warmed to ambient temperature, during which its color slowly changed from purple to green. After being stirred for 18 h, the solution was filtered, and the filtrate was dried in vacuo. The residue was redissolved in 3 mL of toluene, the solution was layered with 10 mL of pentane, and the mixture was cooled to −20 °C to deposit dark blue crystals. The product (TTP)Sn(C≡CPh)$_2$ was isolated via filtration, washed with 2 mL of hexanes, and dried in vacuo (0.040 g, 44%). ^{1}H NMR of **10** (C_6D_6, ppm): 9.21 (s, 8H, β-H), 8.02 (d, 8H, $-C_6H_4$-Me), 7.23 (d, 8H, $-C_6H_4$Me), 6.14 (t, 2H, −C≡C*Ph*), 6.01 (t, 4H, −C≡C*Ph*), 5.38 (d, 4H, −C≡C*Ph*), 2.38 (s, 12H, $-C_6H_4$Me). UV−vis (toluene): 419, 441 (Soret), 585, 629 nm. Anal. Calcd for (TTP)Sn(C≡CPh)$_2$ [$SnC_{64}H_{46}N_4$]: C, 77.66; H, 4.68; N, 5.66. Found: C, 77.10; H, 4.98; N, 5.33.

Synthesis of *trans*-(TTP)Sn(C≡CSiMe$_3$)$_2$ (11). The procedure was similar to that for the preparation of **10**. To a stirred solution of 67.6 mg of (TTP)$SnCl_2$ (0.0787 mmol) in about 15 mL of toluene at −25 °C was added 22.1 mg of LiC≡C$SiMe_3$ (0.221 mmol). The mixture was warmed to ambient temperature, during which its color slowly changed from purple to green. After 16 h, ^{1}H NMR spectroscopy was used to monitor the extent of reaction. As the reaction was found not to be complete, an additional 14.1 mg of LiC≡C$SiMe_3$ (0.135 mmol) was added to the mixture. After an additional 16 h, the mixture was filtered, and the green filtrate was concentrated to about 2 mL. The solution was then covered with 6 mL of hexanes, and the mixture was cooled to −25 °C. Complex **11** was isolated via filtration, washed with 2 mL of hexanes, and dried in vacuo (30 mg, 39%). ^{1}H NMR of **11** (C_6D_6, ppm): 9.16 (s, 8H, β-H), 8.05 (d, 8H, $-C_6H_4$Me), 7.26 (d, 8H, $-C_6H_4$Me), 2.39 (s, 12H, $-C_6H_4$Me), −1.26 (s, 18H, $-SiMe_3$). UV−vis (toluene): 419, 441 (Soret), 585, 629 nm. Anal. Calcd for (TTP)Sn(C≡C$SiMe_3$)$_2$ [$SnC_{58}H_{54}N_4Si_2$]: C, 70.94; H, 5.54; N, 5.71. Found: C, 70.90; H, 6.04; N, 5.65.

Synthesis of *trans*-(TTP)Sn(C≡CPh)(OMe) (12). To a stirred solution of (TTP)Sn(C≡CPh)$_2$ (0.0315 g, 0.0318 mmol) in 7 mL of C_6H_6 was added 86.4 μL a of C_6H_6 solution of MeOH (0.0118 g in 1.0 mL of C_6H_6) (about 0.0318 mmol). After 3 h, the green solution was brought to dryness in vacuo, and the residue was redissolved in about 1 mL of C_6H_6. This solution was then mixed with about 8 mL of hexanes, and the mixture was cooled to −25 °C to deposit microcrystals. Complex **12** was isolated via filtration, washed with 1 mL of hexanes, and dried in vacuo (0.015 g, 51%). ^{1}H NMR of *trans*-(TTP)Sn(C≡CPh)(OMe) (C_6D_6, ppm): 9.19 (s, 8H, β-H), 8.03 (d, 4H, $-C_6H_4$Me), 7.95 (d, 4H, $-C_6H_4$Me), 7.23 (m, 8H, $-C_6H_4$Me), 6.14 (t, 1H, −C≡C*Ph*), 6.00 (t, 2H, −C≡C*Ph*), 5.41 (d, 2H, −C≡C*Ph*), 2.38 (s, 12H, $-C_6H_4$Me), −1.53 (s, 3H, −O*Me*). UV−vis (toluene): 414, 435 (Soret), 573, 615 nm. MS (NH_3/CI, negative): *m*/*z* 919.7 (M^- 919.7).

Reaction of (TTP)Sn(C≡CPh)$_2$ (10) with MeOH. In air at ambient temperature, 4.2 mg of (TTP)Sn(C≡CPh)$_2$ (0.004 mmol) was added to a NMR tube and dissolved in about 0.7 mL of C_6D_6. Then 3.0 μL

Table 1. Selected Crystallographic Data for the Structure Determination of(TTP)Sn(C≡CPh)$_2$

empirical formula	$C_{64}H_{46}N_4Sn$
temperature	293(2) K
crystal system	monoclinic
space group	$P2_1/c$
a	10.9424(2) (Å)
b	14.5565(5) (Å)
c	16.4968(6) (Å)
α	90°
β	100.7930(10)°
γ	90°
Z	2
density	1.273 Mg/m^3
θ range for data collection	1.88−28.26°
goodness-of-fit on F^2	1.035
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0353$; w$R_2 = 0.0890$
R indices (all data)	$R_1 = 0.0584$; w$R_2 = 0.0996$

of MeOH was added to the solution. The reaction was monitored with ^{1}H NMR spectroscopy. It was found that, in 1 h, complex **10** was completely converted to *trans*-(TTP)Sn(C≡CPh)(OMe) (**12**). After 4.5 h, complex **12** disappeared, and the only porphyrin complex in the solution was (TTP)Sn(OMe)$_2$ (**13**). The ^{1}H NMR spectrum of *trans*-(TTP)Sn(C≡CPh)(OMe) in this solution with excess MeOH exhibited resonances at 9.20 (s, 8H, β-H), 8.14 (d, 4H, −C$_6$*H*$_4$Me), 8.04 (d, 4H, −C$_6$*H*$_4$Me), 7.27 (m, 8H, −C$_6$*H*$_4$Me), 6.14 (t, 1H, −C≡C*Ph*), 5.99 (t, 2H, −C≡C*Ph*), 5.40 (d, 2H, −C≡C*Ph*), 2.39 (s, 12H, −C$_6$H$_4$*Me*), and −1.80 ppm (s, 3H, −O*Me*). Similarly, the ^{1}H NMR spectrum of (TTP)Sn(OMe)$_2$ in this solution (with excess MeOH) contained peaks at 9.20 (s, 8H, β-H), 8.11 (d, 8H, −C$_6$*H*$_4$Me), 7.28 (d, 8H, −C$_6$*H*$_4$Me), 2.40 (s, 12H, −C$_6$H$_4$*Me*), and −1.59 ppm (s, 6H, −O*Me*). ^{1}H NMR of isolated (TTP)Sn(OMe)$_2$ (C$_6$D$_6$, ppm): 9.17 (s, 8H, β-H), 7.95 (d, 8H, −C$_6$*H*$_4$Me), 7.23 (d, 8H, −C$_6$*H*$_4$Me), 2.38 (s, 12H, −C$_6$H$_4$*Me*), −1.38 (s, 6H, −O*Me*). ^{1}H NMR of (TTP)Sn(OMe)$_2$ (CDCl$_3$), ppm: 9.11 (s, 8H, β-H), 8.19 (d, 8H, −C$_6$*H*$_4$Me), 7.60 (d, 8H, −C$_6$*H*$_4$Me), 2.72 (s, 12H, −C$_6$H$_4$*Me*), −2.16 (s, 6H, −O*Me*). These values are identical to the reported ^{1}H NMR data.[22]

X-ray Structure Determination of (TTP)Sn(C≡CPh)$_2$ (10). A crystal suitable for X-ray structure analysis was grown in a toluene solution layered with hexanes at ambient temperature. A dark-blue needlelike crystal of (TTP)Sn(C≡CPh)$_2$ of approximate dimensions of 0.60 mm × 0.15 mm × 0.15 mm was used for X-ray crystallographic analysis. Intensity data were measured at 293 °C on a standard Siemens SMART1000 CCD-based X-ray diffractometer system equipped with a Mo-target X-ray tube (λ = 0.710 73 Å) operating at 2000 W. The detector was placed at a distance of 5.016 cm from the crystal.

A total of 1260 frames were collected with a scan width of 0.3° in ϕ and an exposure time of 30 s/frame. The frames were integrated with the Siemens SAINT software package using a narrow-frame integration algorithm. The integration of the data using a monoclinic unit cell yielded a total of 13 041 reflections to a maximum 2θ angle of 56.5° (0.75 Å resolution), of which 5454 were independent (redundancy 2.39, $R_{int} = 2.95\%$, $R_{sig} = 3.96\%$) and 4289 (78.6%) were greater than $4\sigma(F)$. The final cell constants are based upon the refinement of the (x, y, z) centroids of 8192 reflections above $2\sigma(I)$. Analysis of the data were corrected for absorption using the SADABS program with minimum and maximum transmission coefficients of 0.625 and 0.862, respectively.

The structure was solved and refined using the Siemens SHELXTL (version 5.1) software package. The final anisotropic full-matrix least-squares refinement on F^2 for data to $2\theta < 55°$ converged at $R_1 = 3.53\%$ and wR_2 = 8.90%. Selected crystallographic data for the crystal structure determination of **10** are shown in Table 1.

Results and Discussion

Synthesis and Characterization of Bis(amido)tin Porphyrins. Lithium amide reagents have been used to prepare early transition metal (Ti, Zr, etc.) amido complexes with porphyrin and other macrocyclic ligands.[17,23] A similar strategy was used here to prepare bis(amido)tin porphyrins. When (TTP)SnCl$_2$ was treated with more than 2 equiv of LiNHPh and LiNPh$_2$ in toluene, respectively, bis(amido) complexes **1** and **2** were formed (eqs 1 and 2). These two compounds are readily identified as

$$(TTP)SnCl_2 + 2LiNHPh \rightarrow \underset{\mathbf{1}}{(TTP)Sn(NHPh)_2} + 2LiCl \quad (1)$$

$$(TTP)SnCl_2 + 2LiNPh_2 \rightarrow \underset{\mathbf{2}}{(TTP)Sn(NPh_2)_2} + 2LiCl \quad (2)$$

the trans derivatives by ^{1}H NMR spectroscopy. The *o*- and *m*-protons of the *meso*-tolyl groups each appear as doublets, indicating that a mirror plane of symmetry is coincident with the porphyrin macrocycle. The aromatic proton resonances of the coordinated phenylamido group of **1** appear at 5.87 (6H, *m*-, *p*-H) and 2.34 ppm (4H, *o*-H), and the resonance of the NH proton appears at −4.37 ppm. These strong upfield shifts are a result of the shielding effect of the porphyrin ring. Similarly, the protons of the coordinated diphenylamido group of **2** also appear upfield as two triplets at 6.15 (*p*-H) and 6.01 ppm (*m*-H) and a doublet at 2.91 ppm (*o*-H). These upfield chemical shifts are diagnostic for axial ligands bound to the metalloporphyrin.[17] The chemistry of tin is notably different from that of titanium. When (TTP)SnCl$_2$ was treated with 1 equiv of LiNPh$_2$, only bis(amido) complex **2** was detected. No mono(amido) complex (TTP)Sn(NPh$_2$)Cl was observed. In contrast, (TTP)Ti(NPh$_2$)Cl could be isolated under the same conditions.[17] Moreover, during the preparation of **1**, no imido complex was detected when more than 2 equiv of LiNHPh were used. Similar conditions for the Ti analogue only produced the imido complex (TTP)Ti=NPh.[17] This indicates that tin is not capable of forming π-bonds with the axial ligand.

When the bulky lithium salt (lithium (2,4,6-tri-*tert*-butylphenyl)amide) was employed, no bis(amido) complex was formed. Only the reduced product (TTP)Sn was detected (reaction 3). Even at low temperature (−78 °C), the main

$$(TTP)SnCl_2 + LiNHR \rightarrow (TTP)Sn \quad (3)$$

R = 2,4,6-tri-*tert*-butylphenyl

product detected was (TTP)Sn. The bulkiness of the amido group appears to prevent nitrogen from binding to Sn as an axial ligand, thus promoting reduction of Sn(IV) to Sn(II). Note that the reducing ability of Li[*t*-BuNH] reportedly caused the formation of Ti(III) products during the treatment of TpTiCl$_3$ with Li[*t*-BuNH] (Tp = hydrotris(3,5-dimethylpyrazolyl)borato anion).[24]

When *o*-C$_6$H$_4$(NHLi)$_2$ was used as the amido reagent, the *o*-phenylenebis(amide) complex **3** was formed (eq 4). The ligand-enforced cis coordination geometry is confirmed by ^{1}H

$$(TTP)SnCl_2 + o\text{-}C_6H_4(NHLi)_2 \rightarrow \underset{\mathbf{3}}{(TTP)Sn(o\text{-}C_6H_4(NH)_2)} + 2LiCl \quad (4)$$

NMR spectroscopy. The lack of mirror symmetry coincident with the porphyrin ring in **3** is shown by the nonequivalence of

(22) Tsai, C.-C.; Chen, Y.-J.; Chen, J.-H.; Hwang, L.-P. *Polyhedron* **1992**, *11*, 1647.

(23) Nikonov, G. I.; Blake, A. J.; Mountford, P. *Inorg. Chem.* **1997**, *36*, 1107.

(24) Dunn, S. C.; Mountford, P.; Shishkin, O. V. *Inorg. Chem.* **1996**, *35*, 1006.

the *ortho* protons of the *meso*-tolyl groups. These protons appear as two broad resonances at 8.00 and 7.89 ppm. The NH signal of the coordinated amides resonates at −1.38 ppm. This is downfield relative to the amide protons of **1** and indicates that the NH groups in **3** are further from the centroid of the porphyrin ring.[25] When PhNLiNLiPh was used, the corresponding azobenzene complex was not formed. Instead, only the reduced product (TTP)Sn and azobenzene were formed (eq 5). In addition, no reaction occurs between (TTP)Sn and PhN═NPh in C_6D_6 at ambient temperature and at 80 °C. This indicates that (TTP)Sn(η^2-PhNNPh) is not thermodynamically stable with respect to (TTP)Sn and PhN═NPh.

$$(TTP)SnCl_2 + PhNLiNLiPh \rightarrow (TTP)Sn + PhN{=}NPh + 2LiCl \quad (5)$$

Ligand Exchange of 1 with Amines. The phenylamido complex (TTP)Sn$(NHPh)_2$ can react with other amines to form new bis(amido)tin porphyrins (eq 6). When (TTP)Sn$(NHPh)_2$ was treated with a 10-fold excess of *p*-toluidine, (TTP)Sn[NH-(*p*-C_6H_4Me)]$_2$ (**4**) formed, but the conversion was not complete even at elevated temperature (80 °C) as monitored by ^{1}H NMR spectroscopy. When 2,3,5,6-tetrafluoroaniline ($NH_2(C_6F_4H)$) was used, complex **1** was completely converted to (TTP)Sn-($NH(C_6F_4H)$)$_2$ (**5**) at ambient temperature. There was no reaction between **1** and 2,4,6-tri-*tert*-butylaniline, even at high temperature. There was also no reaction between **1** and 2,4,6-trimethylaniline. The lability of the amido complexes correlates directly with the basicity of the axial ligands. The amide exchange in eq 6 is governed by simple acid/base chemistry. The most basic amide prefers to form the neutral amine.

$$(TTP)Sn(NHPh)_2 + 2NH_2R \rightarrow \underset{\mathbf{4},\ \mathbf{5}}{(TTP)Sn(NHR)_2} + 2NH_2Ph \quad (6)$$

4: R = *p*-methylphenyl

5: R = 2,3,5,6-tetrafluorophenyl

Chelation can also be used to drive amide exchange. When (TTP)Sn$(NHPh)_2$, **1**, is treated with *o*-$C_6H_4(NH_2)_2$ in C_6D_6, conversion of **1** to (TTP)Sn(*o*-$C_6H_4(NH)_2$), **3**, is complete in 6 h. This process is conveniently monitored by ^{1}H NMR. The β-H signal for the starting bis(amide) **1** at 9.08 ppm is replaced by a new signal at 9.11 ppm corresponding to the β-H resonance for the new *o*-phenylenedamide complex **3**. Diagnostic upfield-shifted resonances for the coordinated *o*-$C_6H_4(NH)_2$ ligand appear at 5.74 (m, 2H, *o*-H), 4.94 (m, 2H, *m*-H), and 1.38 ppm (s, 2H, NH). However, treatment of (TTP)Sn$(NHPh)_2$ with 2.4 equiv of PhNH−NHPh in C_6D_6 results in the production of (TTP)Sn^{II} and 2 equiv of aniline. The amount of azobenzene could not be quantified by ^{1}H NMR due to the overlap of its resonances with the porphyrin tolyl proton and aniline signals. This reaction is analogous to eq 5 and reflects the thermodynamic instability of a Sn(II) η^2-azobenzene complex.

$$(TTP)Sn(NHPh)_2 + PhHN{-}NHPh \rightarrow (TTP)Sn^{II} + PhN{=}NPh + H_2NPh \quad (7)$$

Characterization of Tin Porphyrins with σ-Bonded Carbon−Tin Axial Ligands. Three different methods have been reported for the synthesis of σ-bonded metalloporphyrins. The first involved a metathetical reaction of (por)MCl, (por)MCl_2, or (por)$M(OH)_2$ with a carbanion source.[5,6,9,11,26] The second used oxidative addition of an alkyl or aryl halide to a low-valent metalloporphyrin complex. The third method employed a direct metalation of Li_2(por) with an aryltin reagent, Ph_2SnCl_2.[11] In this study, related routes were used to prepare alkyltin porphyrins. The diethyl complex (TTP)$SnEt_2$ (**6**) was synthesized and isolated via the reaction of (TTP)$SnCl_2$ with $ZnEt_2$ at low temperature, as shown in eq 8. Complex **6** slowly decomposes to form unidentified products at ambient temperature. The neopentyl analogue, (TTP)Sn$(CH_2CMe_3)_2$ (**7**), was detected during the reaction of (TTP)$SnCl_2$ with the lithium salt $LiCH_2$-CMe_3 at low temperature (eq 9) and was not isolated cleanly due to decomposition. The A_2B_2 splitting pattern for the tolyl protons in the ^{1}H NMR spectra for **6** and **7** indicates that they are trans-derivatives. The resonances of the methylene protons of the axial ligands in **6** and **7** occur at −6.24 and −6.65 ppm, respectively, indicating the close proximity of these protons to the porphyrin centroid. This is expected for an alkyl group σ-bonded to a main group metal of a metalloporphyrin, including the unstable (por)$Sn(R)_2$ (R = Et, Pr, *i*-Pr, Me_3SiCH_2, etc.).[9,26]

$$(TTP)SnCl_2 + ZnEt_2 \rightarrow \underset{\mathbf{6}}{(TTP)SnEt_2} + ZnCl_2 \quad (8)$$

$$(TTP)SnCl_2 + 2LiCH_2CMe_3 \rightarrow \underset{\mathbf{7}}{(TTP)Sn(CH_2CMe_3)_2} + 2LiCl \quad (9)$$

The products produced from the reaction between (TTP)-$Li_2(THF)_2$ and 1 equiv of Me_2SnBr_2 are solvent dependent. In toluene, the product is *cis*-(TTP)$SnMe_2$ (**8**) (eq 10). This result is analogous to the preparation of *cis*-(por)$SnPh_2$.[11] The nonequivalence of the *ortho* protons of the *meso* aryls on the ring in complex **8**, as shown by the two broad resonances at 8.14 and 7.93 ppm respectively, supports the cis geometry of the two axial methyl groups. Moreover, this geometry is supported by the proton resonance of the axial methyl ligands. The methyl protons appear at −3.83 ppm, which is further downfield than resonances of typical axial alkyl ligands (usually less than −5 ppm).[5,6] In contrast, the transient intermediate *trans*-(TTP)$SnMe_2$ detected via the reaction of (TTP)$SnCl_2$ with LiMe exhibits the proton resonance of the methyl ligands at −6.46 ppm. Solid complex **8** shows detectable decomposition at ambient temperature in several hours, even in the dark.

$$(TTP)Li_2(THF)_2 + Me_2SnBr_2 \xrightarrow{\text{toluene}} \underset{\mathbf{8}}{\textit{cis}\text{-}(TTP)SnMe_2} + 2LiBr + 2THF \quad (10)$$

When (TTP)$Li_2(THF)_2$ is treated with Me_2SnBr_2 in CH_2Cl_2, the new product *trans*-(TTP)$Sn(CH_3)Br$ is formed (reaction 11). The ^{1}H NMR and UV−vis spectroscopy of complex **9** are quite similar to that of *trans*-(TTP)$Sn(CH_3)I$.[10] The trans geometry is supported by the methyl proton ^{1}H NMR signal located at −5.68 ppm, which was upfield compared to that of **8**. Solid complex **9** also slowly decomposes at ambient temperature.

$$(TTP)Li_2(THF)_2 + Me_2SnBr_2 \xrightarrow{CH_2Cl_2} \underset{\mathbf{9}}{(TTP)SnMeBr} \quad (11)$$

(25) Jenson, T. R.; Katz, J. J. In *The Porphyrins*; Dolphin, D., Ed.; Academic: New York, 1978; Vol. 4, Chapter 5.

(26) Cloutour, C.; Debaig-Valade, C.; Gacherieu, C.; Pommier, J.-C. *J. Organomet. Chem.* **1984**, *269*, 239.

The acetylide complexes (TTP)Sn(C≡CPh)$_2$ (**10**) and (TTP)-Sn(C≡CSiMe$_3$)$_2$ (**11**) were isolated via the reaction of (TTP)-SnCl$_2$ with the corresponding alkynyllithium salt (eq 12). The

$$(\mathrm{TTP})\mathrm{SnCl_2} + 2\mathrm{LiR} \rightarrow \underset{\mathbf{10},\ \mathbf{11}}{(\mathrm{TTP})\mathrm{Sn(R)_2}} + 2\mathrm{LiCl} \quad (12)$$

$$\mathrm{R} = \mathrm{C{\equiv}CPh}\ (\mathbf{10}),\ \mathrm{C{\equiv}CSiMe_3}\ (\mathbf{11})$$

alkynyl ligands are mutually trans, as indicated by the A_2B_2 splitting pattern for the tolyl groups in the NMR spectra. This trans coordination geometry was also established by the molecular structure of **10** (vide infra). The resonances of protons of the axial groups in **10** and **11** appear upfield due to the shielding effect of the porphyrin ring current. These two compounds are inert at ambient temperature and are not light sensitive. Even in air, the benzene solutions of **10** and **11** showed negligible decomposition in 3 days.

Reaction of (TTP)Sn(C≡CPh)$_2$ (10) with MeOH. When treated with MeOH, complex **10** could be smoothly converted in a stepwise manner first to (TTP)Sn(C≡CPh)(OMe) (**12**) and then subsequently to (TTP)Sn(OMe)$_2$ (**13**), as shown in eqs 13 and 14. The characterization of (TTP)Sn(OMe)$_2$ was reported previously.[22]

$$\underset{\mathbf{10}}{(\mathrm{TTP})\mathrm{Sn(C{\equiv}CPh)_2}} + \mathrm{MeOH} \rightarrow \underset{\mathbf{12}}{(\mathrm{TTP})\mathrm{Sn(C{\equiv}CPh)(OMe)}} + \mathrm{PhC{\equiv}CH} \quad (13)$$

$$\underset{\mathbf{12}}{(\mathrm{TTP})\mathrm{Sn(C{\equiv}CPh)(OMe)}} + \mathrm{MeOH} \rightarrow \underset{\mathbf{13}}{(\mathrm{TTP})\mathrm{Sn(OMe)_2}} + \mathrm{PhC{\equiv}CH} \quad (14)$$

When the bis(amido) complex **1** (0.0025 g, 0.0026 mmol) was treated with a large excess of MeOH (0.0136 g, 0.42 mmol) in C_6D_6 in a NMR tube at ambient temperature, the color of solution immediately changed to purple and the ^{1}H NMR spectrum indicated that complex **1** was cleanly converted to (TTP)Sn(OMe)$_2$ (eq 15). In addition, when complex **10** (0.0052 g, 0.0052 mmol) was treated with 2,3,5,6-tetrafluoroaniline (0.0036 g, 0.028 mmol) in C_6D_6 at ambient temperature, no reaction was detected after 23 h via ^{1}H NMR spectroscopy (reaction 16). The substitution chemistry described here reveals

$$\underset{\mathbf{1}}{(\mathrm{TTP})\mathrm{Sn(NHPh)_2}} + 2\mathrm{MeOH} \rightarrow \underset{\mathbf{13}}{(\mathrm{TTP})\mathrm{Sn(OMe)_2}} + 2\mathrm{PhNH_2} \quad (15)$$

$$\underset{\mathbf{10}}{(\mathrm{TTP})\mathrm{Sn(C{\equiv}CPh)_2}} + 2,3,5,6\text{-}\mathrm{C_6F_4HNH_2} \rightarrow \text{no reaction} \quad (16)$$

that the ligand affinity for tin(IV) porphyrins increases in the order:

$$\mathrm{NR_1R_2} < \mathrm{C{\equiv}CPh},\ \mathrm{C{\equiv}CSiMe_3} < \mathrm{OMe}$$

This trend correlates well with the decreased basicity of NH_2^- (or $NR_1R_2^-$) > $HC{\equiv}C^-$ (or $RC{\equiv}C^-$) > OR^-.[27] The lability of complexes **6**−**8** at ambient temperature also seems to be related to the strong basicity of the axial alkyl ligands. Decreasing the basicity of the alkyl ligands seems to increase the inertness of the dialkyltin porphyrin complexes.

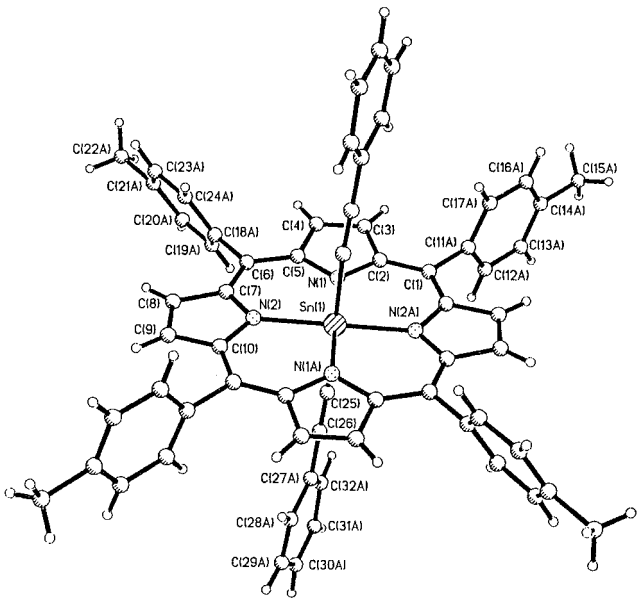

Figure 1. Perspective view of complex **10** showing the selected atom-numbering scheme.

X-ray Crystal Structure of 10. In the crystal structure of **10**, each unit cell contains two molecules in the space group $P2_1/c$. The coordination geometry of (TTP)Sn(C≡CPh)$_2$ is shown in Figure 1. This molecule has a pseudooctahedral structure with the two phenylacetylide groups at mutually trans position. The molecule is centrosymmetric, and the Sn and four N atoms are coplanar. Selected bond lengths and bond angles are listed in Table 2.

The two independent Sn−N bond distances of **10** are equal within experimental error at 2.115(2) and 2.119(2) Å, respectively. These distances are slightly greater than the Sn−N bonds in other tin(IV) porphyrin complexes (Sn−N in Sn(TPP)F$_2$ 2.056(7) and 2.071(6) Å. Sn−N in Sn(TPP)(NO$_3$)$_2$ 2.075(5) and 2.080(5) Å),[2,3] but are smaller than those in *trans*-Sn(TPP)-Ph$_2$(CH$_2$Cl$_2$) (Sn−N (average) 2.134 Å).[11] The two Sn−C bond distances in **10** are identical at 2.167(2) Å and are slightly shorter than the Sn−C bond distances of 2.196(4) and 2.212(4) Å in Sn(TPP)Ph$_2$(CH$_2$Cl$_2$).[11] The Sn−C distance in **10** is also comparable to the Sn−C distances in other tin complexes, such as [Me$_3$Sn(NH$_3$)$_2$][N(SO$_2$Me)$_2$] (Sn−C 2.124(2)−2.117(2) Å),[28] [C$_6$H$_5$)$_3$SnC$_6$H$_2$(CF$_3$)$_3$] (Sn−C 2.145(8)−2.233(7) Å),[29] [(CH$_3$)$_3$-SnOC(CF$_3$)$_2$]$_2$C$_6$F$_4$ (Sn−C 2.097(19)−2.134(23) Å)[30] and (CH$_3$)$_2$-Sn[N(SO$_2$CH$_3$)$_2$]$_2$ (Sn−C 2.101(3)−2.108(3) Å),[30] although their coordination geometries are different. The Sn−C distance in **10** is also comparable to the sum of the covalent radii (2.177 Å) of Sn (1.405 Å) and C (0.772 Å).[31] This indicates that the Sn−C bond in **10** is essentially a σ-bond. The acetylenic bond distance for C(25)−C(26) of 1.197(3) Å is consistent with a triple C≡C bond and is comparable to the C≡C bond distance

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Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) in Complex **10**

Sn(1)−N(2A)	2.115(2)	Sn(1)−N(2)	2.115(2)
Sn(1)−N(1)	2.119(2)	Sn(1)−N(1A)	2.119(2)
Sn(1)−C(25)	2.167(2)	Sn(1)−C(25)#1	2.167(2)
C(25)−C(26)	1.197(3)	C(26)−C(27A)	1.440(3)
N(2A) −Sn(1)−N(2)	180.0	N(2A) −Sn(1)−N(1)	89.96(7)
N(2)−Sn(1) −N(1)	90.04(7)	N(2A) −Sn(1)−N(1A)	90.04(7)
N(2)−Sn(1) −N(1A)	89.96(7)	N(1)−Sn(1) −N(1A)	180.0
N(2A) −Sn(1)−C(25)#1	88.66(8)	N(2)−Sn(1) −C(25)#1	91.34(8)
N(1)−Sn(1) −C(25)#1	87.45(8)	N(1A) −Sn(1)−C(25)#1	92.55(8)
N(2A) −Sn(1)−C(25)	91.34(8)	N(2)−Sn(1) −C(25)	88.66(8)
N(1)−Sn(1) −C(25)	92.55(8)	N(1A) −Sn(1)−C(25)	87.45(8)
C(25)−Sn(1) −C(25)#1	180.0	C(25)−C(26) −C(27A)	178.5(3)
C(26)−C(25) −Sn(1)	170.1(2)	C(28)−C(27A) −C(26)	123.6(6)
C(32A) −C(27A) −C(26)	118.3(5)		

of 1.187(7) Å in *trans*-[$(NH_3)Ru(C{\equiv}CPh)(Ph_2PCH_2CH_2PPh_2)_2$]-$PF_6$.[32] Very little, if any, π-bonding exists between the acetylide ligands and Sn metal center. The angles of C(25)−C(26)−C(27A) and C(26)−C(25)−Sn(1) are 170.1(2) and 178.5(3)°, respectively, indicative of a slight distortion around the tin coordination center.

Conclusion

In this work we have demonstrated that bis(amido)tin porphyrins, including (TTP)Sn$(NHPh)_2$, (TTP)Sn$(NPh_2)_2$, and (TTP)Sn(*o*-$C_6H_4(NH)_2$), and dialkyltin porphyrins, including (TTP)Sn$(C{\equiv}CPh)_2$ and (TTP)Sn$(C{\equiv}CSiMe_3)_2$, can be isolated via the reactions of (TTP)$SnCl_2$ with related lithium amide and alkyllithium salts. This is a new route for the synthesis robust dialkyltin porphyrins. With the reaction of (TTP)$SnCl_2$ with $ZnEt_2$ and the reactions of Li_2(TTP)$(THF)_2$ with Me_2SnBr_2 in different solvents at low temperatures, labile (TTP)$SnEt_2$, *cis*-(TTP)$SnMe_2$, and *trans*-(TTP)SnMeBr could be synthesized. The X-ray structure of (TTP)Sn$(C{\equiv}CPh)_2$ shows the trans coordination geometry of the complex. It is also found that the stability of these tin porphyrins is well related to the basicity of the axial group.

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