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

Abstract
Treatment of (TTP)SnCl₂ (TTP = meso-tetra-p-tolyporphyrinato dianion) with an excess of lithium amides (LiNPh, LiNPh₂, o-C₆H₄(NHLi)₂) affords the metathesis products (TTP)Sn(NHPh)₂ (1), (TTP)Sn(NPh₂)₂ (2), and (TTP)Sn(o-C₆H₄(NH)₂) (3). Ligand exchanges of 1 with p-toluidine and 2,3,5,6-tetrafluoroaniline afford the complexes (TTP)Sn(p-NHC₆H₄Me)₂ (4) and (TTP)Sn(NHC₆F₄H)₂ (5), respectively. Treatment of (TTP)SnCl₂ 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–NPh results in the production of (TTP)Sn, azobenzene, and aniline. The diethyl complex (TTP)SnEt₂ (6) can be prepared via the reaction of (TTP)SnCl₂ with 1 equiv of ZnEt₂. The dineopentyl complex (TTP)Sn(CH₂CMe₃)₂ (7) can be detected in the reaction of (TTP)SnCl₂ with neopentyllithium. The methyl derivatives cis-(TTP)SnMe₂ (8) and (TTP)SnMeBr (9) can be obtained by the treatment of (TTP)Li₂(THF)₂ with 1 equiv of Me₂SnBr₂ at low temperature in toluene and CH₂Cl₂, respectively. Treatment of (TTP)SnCl₂ with an excess of alkynyllithium salts (LiC⋮CPh, LiC⋮C₃SiMe₃) affords the metathesis products (TTP)Sn(C⋮CPh)₂ (10) and (TTP)Sn(C⋮C₃SiMe₃)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, P2₁/c, a = 10.9424(2) Å, b = 14.5565(5) Å, c = 16.4968(6) Å, α = 90°, β = 100.7930(10)°, γ = 90°, R₁ = 3.53%, and wR₂ = 8.90%) was determined from X-ray diffraction data.

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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)SnCl₂ (TTP = meso-tetra-p-tolylporphyrinato dianion) with an excess of lithium amides (LiNPh₂, LiN₆H₄(NH)₂Cl₂) affords the metathesis products (TTP)Sn(NN₆H₄(NH)₂) (1), (TTP)Sn(NN₆H₄(NH)₂Cl) (2), and (TTP)Sn(o-C₆H₄(NH)₂) (3). Ligand exchanges of 1 with p-toluidine and 2,3,5,6-tetrafluoroaniline afford the complexes (TTP)Sn(p-NH₄C₆H₄Me)₂ (4) and (TTP)Sn(N(C₆F₄H)₂) (5), respectively. Treatment of (TTP)SnCl₂ with the bulky lithium (2,4,6-tri-tert-butylylamide) or with PhNLLiPh does not form the corresponding amido or azobenzene complexes but produces the reduced product (TTP)Sn. In addition, the reaction of (TTP)Sn(NH₄Cl)₂ with PhHN—NHPh results in the production of (TTP)Sn, azobenzene, and aniline. The diethyl complex (TTP)SnEt₂ (6) can be prepared via the reaction of (TTP)SnCl₂ with 1 equiv of ZnEt₂. The dineopentyl complex (TTP)Sn(CH₂CMe₃)₂ (7) can be detected in the reaction of (TTP)SnCl₂ with neopentyl lithium. The methyl derivatives cis-(TTP)SnMe₂ (8) and (TTP)SnMeBr (9) can be obtained by the treatment of (TTP)L₂(THF)₂ with 1 equiv of Me₂SnBr₂ at low temperature in toluene and CH₂Cl₂, respectively. Treatment of (TTP)SnCl₂ with an excess of alkynyllithium salts (LiC≡CpH, LiC≡CSiMe₃) affords the metathesis products (TTP)Sn(C≡CpH)₂ (10) and (TTP)Sn(C≡CSiMe₃)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, P2₁/c; α = 10.9424(2) Å, β = 14.5565(5) Å, c = 16.4968(6) Å, α = 90°, β = 100.7930(10)°, γ = 90°, R₁ = 3.53%, and wR₂ = 8.90%) was determined from X-ray diffraction data.

Introduction

In tin porphyrin chemistry, many derivatives of general formula Sn(por)L₁L₂ (por = general porphyrin dianion; L₁, L₂ = F, Cl, OR, OH, N₃, etc.) have been synthesized and well characterized. However, robust tin metalloporphyrins 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(R₂) (R = alkyl, aryl; M = Al, Ga, 5,6 Si, Ge) that have been synthesized and described in the literature. Diallyl tin 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 O₂ sensitivity. The first porphyrin complexes containing an inert tin–carbon bond were synthesized by Kadish et al. by oxidative addition of MeI to SnII(por). The only other thermally robust but light sensitive dialkyltin porphyrin complexes of types cis- and trans-Sn(por)Cl₂ were reported in 1996. The cis complex was prepared by transmetalating Li₂(por)(OE₂) with SnPh₂Cl₂. The trans derivative was produced by the reaction of Sn(por)Cl₂ with Ph₂Mg. The only characterized amidotin porphyrin complex is bis(phenyltetrazolato)tin(IV) tetra-p-tolylporphyrinate. 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. Previous studies have shown that tin porphyrins could be used to inhibit bilirubin synthesis and to prevent jaundice, a common illness in neonates. 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. This in paper, the synthesis of several bis(amido)tin(IV) porphyrins and a series of tin(IV)–carbon σ-bonded porphyrins

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, OEt2, C6D6, and toluene were dried over pure solutions of Na/benzophenone, degassed with three "freeze–pump–thaw" cycles, and stored in the glovebox before being vacuum-transferred. CH2Cl2 was dried with P2O5, degassed and also stored in the glovebox before being vacuum-transferred. Literature procedures were used to synthesize (TTP)SnCl4, (TTP)Li(THF),LiCNPb,18LiCH3CMe3,19PhNLi-LiPn (N,N′-dilithioheterobenzene),18 and LiNHPh.20 Lithium phenylacetylide and o-C6H4(NHLi)2 were synthesized by the reactions of phenylacetylene and o-diaminobenzene with n-butyllithium (1.6 M BuLi in hexane) in Et2O. Lithium (2,4,6-tri-tert-butylyphenylamine and LiC6F4=CSi(CH3)3 were similarly prepared via the lithiation of 2,4,6-tri-tert-butylicyanilide and (CH3)2Si=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. 1H 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 Siemons, 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)SnCl2 (0.0078 g, 0.0025 mmol) in 15 mL of toluene at −34 °C was added PhNH2Li (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. The (TTP)Sn(NHPh)2 was isolated by filtration, washed with 2 mL of hexanes, and dried in vacuo (0.042 g, 52%). 1H NMR (C6D6 ppm): 9.08 (s, 8H, β-H), 8.01 (d, 8H, –C=HMe), 7.27 (d, 8H, –C=HMe), 5.87 (m, 6H, –NHPh), 2.40 (s, 12H, C6H4Me), 2.34 (m, 4H, –NHPh), –4.37 (s, 2H, –NHPh). UV–vis (toluene): 408, 429 (Soret), 429, 568, 609 nm. Anal. Calcd for (TTP)Sn(NHC6H4Me)2: C, 76.49; H, 5.31; N, 7.90. Found: C, 76.49; H, 5.19; N, 7.90. 1H NMR of PhNNPh (C6D6): 8.01 (d, 8H, β-H), 8.09 (d, 8H, –C=HMe), 7.25 (d, 8H, –C=HMe), 2.40 (s, 12H, –C=HMe), identical to the reported data.11 1H NMR of PhNH2 (C6D6): 8.01 (d, 4H), 7.0–7.18 (m, 6H), identical with the spectroscopy of an authentic sample.

Reaction of (TTP)SnCl2 with Lithium 2,4,6-tri-tert-butylyphenylamide. An NMR tube was charged with (TTP)SnCl2 (0.0343 g, 0.0044 mmol). Lithium 2,4,6-tri-tert-butylyphenylamide (0.0031 g, 0.0012 mmol), and about 0.7 mL of C6D6. After 2 h, an 1H NMR spectrum indicated that the only new product was Sn(TTP) 1H NMR spectrum. Approximately 5% of (TTP)SnCl2 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, 0.0055 mmol), p-toluidine (0.0075 g, 0.063 mmol), and about 0.6 mL of C6D6. After 3.4 h, the only new product detected by 1H NMR was (TTP)Sn(p-NHC6H4Me)2. (4). The ratio of (TTP)Sn(p-NHC6H4Me)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. PhNH2 was also identified. 1H NMR of (TTP)Sn(p-NHC6H4Me)2 (4) (C6D6 ppm): 9.07 (s, 8H, β-H), 8.01 (d, 8H, –C=HMe), 7.29 (d, 8H, –C=HMe), 5.67 (m, 4H, –NHC6H4Me), 2.40 (s, 12H, –C=HMe), 2.34 (s, 4H, –NHC6H4Me), 1.77 (s, 6H, –NHC6H4Me), –4.37 (s, 2H, –NHPh). UV–vis (toluene): 408, 429 (Soret), 568, 613 nm. MS (NH4/CI, negative): m/z 1116.1 (M–NH4)6.

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, 0.0055 mmol), 2,3,5,6-tetrafluoroaniline (0.0031 g, 0.0012 mmol), and about 0.5 mL of C6D6. After 2 h, an 1H NMR spectrum indicated that the only new product was Sn(TTP) 1H NMR spectrum. Approximately 5% of (TTP)SnCl2 was unreacted.

Reaction of (TTP)Sn(NHPh)2 (1) with 2,4,6-Tri-butylylaniline. An NMR tube was charged with (TTP)Sn(NHPh)2 (0.0052 g, 0.0055 mmol), 2,4,6-tri-butylylaniline (0.0031 g, 0.0012 mmol), and about 0.7 mL of C6D6. After 2 h, an 1H NMR spectrum indicated that the only new product was Sn(TTP) 1H NMR spectrum. Approximately 5% of (TTP)SnCl2 was unreacted.

Synthesis of (TTP)Sn(o-C6H4(NH2)2) (3). To a stirred solution of (TTP)SnCl2 (0.0048 g, 0.0022 mmol) in 15 mL of toluene at −34 °C was added solid o-C6H4(NHLi)2 (0.0075 g, 0.063 mmol). The solution was warmed to ambient temperature and stirred for 17 h. By 1H NMR spectroscopy, it was found that about 31% of (TTP)SnCl2 was not reacted. Another 7.0 mg of C6H4(NHLi)2 (0.0058 mmol) was added to the mixture. 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-C6H4(NH2)2) was isolated via filtration and dried in vacuo (0.0220 g, 47%). 1H NMR (C6D6 ppm): 9.11 (s, 8H, β-H), 8.00 (br s, 4H, –C=HMe), 7.89 (br s, 4H, –C=HMe), 7.24 (d, 8H, –C=HMe), 5.74 (m, 2H, –NHPh), 4.94 (m, 2H, –NHPh), 2.38 (s, 12H, C6H4Me), –1.38 (s, 2H, C6H4NH). UV–vis (toluene): 430 (Soret), 562, 606 nm. MS (NH4/CI, negative): m/z 893.9 (M–NH4)6.

Reaction of (TTP)SnCl2 with PhNLiLiPh. To an NMR tube were added 0.0088 g of (TTP)SnCl2 (0.010 mmol) and 0.0032 g of PhNLiLiPh (0.016 mmol). About 0.8 mL of C6D6 was also added to the tube. The 1H 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. 1H NMR of (TTP)Sn (C6D6 ppm): 9.19 (s, 8H, β-H), 8.02 (br s, 8H, –C=HMe), 7.25 (d, 8H, –C=HMe), 2.40 (s, 12H, –C=HMe), identical to the reported data.21 1H NMR of PhNNPh (C6D6): 8.01 (d, 4H), 7.0–7.18 (m, 6H), identical with the spectroscopy of an authentic sample.

Reaction of (TTP)SnCl2 with Lithium 2,4,6,4-Tri-tert-butylylaniline. An NMR tube was charged with (TTP)SnCl2 (0.0034 g, 0.004 mmol), lithium 2,4,6,4-tri-tert-butylylanilamide (0.0031 g, 0.0012 mmol), and about 0.7 mL of C6D6. After 2 h, an 1H NMR spectrum indicated that the only new product was Sn(TTP) 1H NMR spectrum. Approximately 5% of (TTP)SnCl2 was unreacted.
(0.005 mmol, 23 μL of a 0.2 M solution), and 0.54 mL of CdMe was added to an NMR tube. Monitoring the reaction by 1H NMR showed it to reach completion in 6 h. 1H NMR peaks observed for (TTP)Sn–(o-C₃H₄HNH) (ppm): 9.11 (8H, β–H), 8.00 (br, 4H, −CH₂Me), 7.89 (br, 4H, −C₆H₅Me), 7.24 (d, 8H, −C₆H₄Me), 7.54 (m, 2H, C₆H₄(ND₃)⁺), 9.49 (m, 2H, C₆H₂Me), 2.38 (s, 12H, CH₂), −1.38 (s, 2H, NH). 1H NMR peaks observed for NH₂Ph (ppm): 7.06 (m, partially obscured) by o-C₃H₄(NH₂)⁺, 6.71 (m, 2H), 6.34 (4H, 2.77 (br, NH).  

### Reaction of (TTP)Sn[NHPh] (1) with PhNH−NHPh. 
In a glovebox, (TTP)Sn[NHPh] (0.0028 g, 0.003 mmol), PhNH−NHPh (1.3 mg, 0.007 mmol) and 0.7 mL of C₆D₆ were added to an NMR tube. After 2 h, the reaction was complete as monitored by 1H NMR. New products observed were (TTP)Sn, NH₂Ph, and PhN−NPh. 1H NMR peaks observed for (TTP)Sn (ppm): 9.18 (s, 8H, β–H), 8.30 (m, −C₆H₅Me, partially obscured by PhNPhH), 7.26 (d, 8H, −C₆H₄Me), 2.40 (s, 12H, CH₂), 2.79 (br, NH). 1H peaks observed for PhN−NPh (ppm): 8.00 (m, partially obscured), 7.14 (m, partially obscured), 7.12 (m, partially obscured).  

### Synthesis of trans-(TTP)SnEt₂ (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)SnCl₂ (0.0071 g, 0.009 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 ZnEt₂ (0.0089 mmol). This solution was kept at −34 °C in a freezer for 23.5 h. The solution was then dried, and the residue was concentrated to 2 mL. The resulting orange-brown solution was maintained at −34 °C, 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 2 mL of toluene, and 5 mL of toluene at 5 °C was added a solution of LiCH₂CMe₃ (0.0018 g, 0.015 mmol) which had been cooled to −34 °C. The solution was warmed to ambient temperature during which its color changed from purple to green. After 16 h, 1H NMR spectroscopy was checked to find that one of the major products corresponded to (TTP)SnMe₂, (TTP)SnMeBr (9). 1H NMR of (TTP)SnMe₂Br (9). To a stirred solution of (TTP)SnCl (0.0784 g, 0.0913 mmol) in 20 mL of toluene at −20 °C was added PhMe=ClLi (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 a 0.2 M solution, and 0.54 mL of C₆D₆ were added to an NMR tube. Monitoring the reaction by 1H NMR showed it to reach completion in 6 h. 1H NMR peaks observed for (TTP)SnMeCl₂ (ppm): 9.21 (s, 8H, β–H), 8.02 (d, 8H, −C₆H₄Me), 7.23 (d, 8H, −C₆H₄Me), 2.38 (s, 12H, −CH₂Me), 5.58 (s, 3H, −CH₃), −1.26 (s, 18H, −SiMe₃). UV–vis (toluene): 419, 441 (Soret), 585, 629 nm. Anal. Calc'd for (TTP)SnMe₂Cl: C₆H₄(NMe₂)₂; C, 77.10; H, 4.98; N, 5.33.  

### Synthesis of trans-(TTP)Sn(C₆H₄Br) (10). 
The following procedure was similar to that for the preparation of 8. To a stirred solution of (TTP)Li(THF) (0.0361 g, 0.0437 mmol) in 10 mL of CHCl₃ at −34 °C was added a solution of SnMe₂Br (0.0127 g, 0.0444 mmol) in 1 mL of CHCl₃ 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 Et₂O, and the mixture was cooled to −34 °C to deposit microcrystals. The product trans-(TTP)SnMe₂Br was isolated by filtration, washed with 1 mL of Et₂O, and dried in vacuo (0.0220 g, 57%). 1H NMR (CdMe ppm): 9.14 (s, 8H, β–H), 8.08 (d, 8H, −C₆H₄Me), 7.87 (d, 8H, −C₆H₄Me), 7.20 (d, 8H, −C₆H₄Me), 2.38 (s, 12H, −CH₂Me), −5.68 (s, 3H, −Me). UV–vis (CHCl₃): 431 (Soret), 565, 608 nm. MS (NH/Cl/positive): m/z: 812.1 (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 [SnC₆H₄(NMe₂)]. 

### Synthesis of trans-(TTP)Sn(C₆H₄Cl) (11). 
The procedure was similar to the preparation for 10. To a stirred solution of 67.6 mg of (TTP)SnCl (0.0787 mmol) in about 15 mL of toluene at −25 °C was added LiMe=ClLi (0.315 mmol). The resulting solution was warmed to ambient temperature, during which its color slowly changed from purple to green. After 16 h, 1H NMR spectroscopy was used to monitor the extent of reaction. As the reaction was found not to be complete, an additional 1.4 mg of LiC₆H₄(SiMe₃) (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 worked up 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%). 1H NMR of 11 (CdMe ppm): 9.16 (s, 8H, β–H), 8.05 (d, 8H, −C₆H₄Me), 7.26 (d, 8H, −C₆H₄Me), 2.39 (s, 12H, −CH₂Me), −1.26 (s, 18H, −SiMe₃). UV–vis (toluene): 419, 441 (Soret), 585, 629 nm. Anal. Calc'd for (TTP)Sn(C₆H₄Cl): C, 77.10; H, 4.98; N, 5.33.  

### Synthesis of trans-(TTP)Sn(C₆H₄(OMe)) (12). 
To a stirred solution of (TTP)Sn(C₆H₄Cl) (0.0315 g, 0.0318 mmol) in 7 mL of C₆H₄Me was added 86.4 μL of a C₂H₄ solution of MeOH (0.018 g in 1 mL of C₆H₄Me) (about 0.0318 mmol). After 3 h, the green solution was brought to dryness in vacuo, and the residue was redisolved in about 1 mL of C₆H₄Me. 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, 5%). 1H NMR of trans-(TTP)Sn(C₆H₄(OMe)) (CdMe ppm): 9.19 (s, 8H, β–H), 8.03 (d, 4H, −C₆H₄Me), 7.95 (d, 4H, −C₆H₄Me), 7.23 (m, 8H, −C₆H₄Me), 6.14 (t, 1H, −C=CPh), 6.00 (t, 2H, −C=CPh), 5.41 (d, 2H, −C=CPh), 2.38 (s, 12H, −CH₂Me), −1.53 (s, 3H, −Me). UV–vis (toluene): 414, 435 (Soret), 573, 615 nm. MS (NH/Cl/negative): m/z: 919.7 (M − 919.7).  

### Reaction of (TTP)Sn(C₆H₄Cl) (10) with MeOH. 
In air at ambient temperature, 4.2 mg of (TTP)Sn(C₆H₄Cl) (0.004 mmol) was added to a NMR tube and dissolved in about 0.7 mL of Cd₂. Then 3.0 μL
Determination of (TTP)Sn(C$_{6}$H$_{4}$)$_{2}$

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</tbody>
</table>

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$_{6}$H$_{4}$)OMe (12). After 4.5 h, complex 12 disappeared, and the only porphyrin complex in the solution was (TTP)SnOMe (13). The $^1$H NMR spectrum of trans-(TTP)Sn(C$_{6}$H$_{4}$)OMe in this solution with excess MeOH exhibited resonances at 9.20 (s, 8H, $H_4$), 7.27 (m, 8H, $H_4$), 6.14 (t, 1H, $H_2$), and 5.94 (t, 2H, $H_2$), 5.40 (d, 2H, $H_2$), 2.39 (s, 12H, $H_2$), and 1.80 ppm (s, 3H, $OMe$). Similarly, the $^1$H NMR spectrum of (TTP)SnOMe in this solution (with excess MeOH) contained peaks at 9.20 (s, 8H, $H_4$), 8.11 (d, 8H, $H_4$), 7.28 (d, 8H, $H_4$), 2.40 (s, 12H, $H_2$), and 1.59 ppm (s, 6H, $OMe$). $^1$H NMR of (TTP)SnOMe (CDCl$_3$), ppm: 9.11 (s, 8H, $H_4$). The integration of the coordinated phenylamido group of 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. 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. Moreover, during the preparation of 1, no imido complex was detected when more than 2 equiv of LiNHP$_2$ were used. Similar conditions for the Ti analogue only produced the imido complex (TTP)Ti=NPh. This indicates that tin is not capable of forming $\pi$-bonds with the axial ligand. When the bulky lithium salt (lithium (2,4,6-tri-tert-butyl-phenyl)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 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(I) to Sn(II). Note that the reducing ability of Li[d-BuNH] reportedly caused the formation of Ti(III) products during the treatment of TpTiCl$_3$ with Li[d-BuNH] (Tp = hydrotris(3,5-dimethylpyrazolyl)borato anion). When $o$-C$_6$H$_4$(NHHLi)$_2$ 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 NMR spectroscopy. The lack of mirror symmetry coincident with the porphyrin ring in 3 is shown by the nonequivalence of the transition metal (Ti, Zr, etc.) amido complexes with porphyrin and other macrocyclic ligands. A similar strategy was used here to prepare bis(amido)tin porphyrins. When (TTP)SnCl$_2$ was treated with more than 2 equiv of LiNHP$_2$ 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$_2$ + 2LiNHP$_2$ → (TTP)Sn(NHP$_2$)$_2$ + 2LiCl (1)  
(TTP)SnCl$_2$ + 2LiNPh$_2$ → (TTP)Sn(NPh)$_2$ + 2LiCl (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 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 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 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.\textsuperscript{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- 

(TTP)SnCl2 + PhNLiNLiPh → (TTP)Sn + PhN=NPPh + 2LiCl \hspace{1cm} (5)

NPh in C6D6 at ambient temperature and at 80 °C. This indicates that (TTP)Sn(n'2-PhNPNPh) is not thermodynamically stable with respect to (TTP)Sn and PhN=NPPh.

**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 is treated with a 10-fold excess of Me2SnBr2 in CH2Cl2, (TTP)Sn(NHMe)2 + 2NH3+ R → (TTP)Sn(NHR)2 + 2NH2Ph \hspace{1cm} (6)

4: R = p-methylphenyl

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

was treated with a 10-fold excess of p-toluidine, (TTP)Sn[NH-(p-C6H4Me)2]2 (4) formed, but the conversion was not complete even at elevated temperature (80 °C) as monitored by 1H NMR spectroscopy. When 2,3,5,6-tetrafluorophenol (NH2(C6F5H)) was used, complex 1 was completely converted to (TTP)Sn(NH(C6F5H)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.

Chelation can also be used to drive amide exchange. When (TTP)Sn(NHPh)2, 1, is treated with o-C6H4(NH)2 in C6D6, conversion of 1 to (TTP)Sn(o-C6H4(NH)2), 3, is complete in 6 h. This process is conveniently monitored by 1H NMR spectroscopy. 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-phenylenediamide complex 3. Diagnostic upfield-shifted resonances for the coordinated o-C6H4(NH)2 ligand appear at 5.74 (m, 2H, β-H), 4.94 (m, 2H, H-m), and 1.38 ppm (s, 2H, NH). However, treatment of (TTP)Sn(NHPh)2 with 2.4 equiv of PhNLiNLiPh in C6D6 results in the production of (TTP)SnII and 2 equiv of aniline. The amount of azobenzene could not be quantified by 1H 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) n2-azobenzene complex.

(TTP)Sn(NHPh)2 + PhHN-→ (TTP)SnII + PhN=NPPh + H2NPh \hspace{1cm} (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)MC1, (por)MC2, or (por)(M=OH)2 with a carbosource.\textsuperscript{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 Li2(por) with an aryltin reagent, Ph2SnCl2.\textsuperscript{11} In this study, related routes were used to prepare alkyltin porphyrins. The diethyl complex (TTP)SnEt2 (6) was synthesized and isolated via the reaction of (TTP)SnCl2 with ZnEt2 at low temperature, as shown in eq 8. Complex 6 slowly decomposes to form unidentified products at ambient temperature. The neopentyl analogue, (TTP)Sn(CH2CMe3)2 (7), was detected during the reaction of (TTP)SnCl2 with the lithium salt LiCH2-CMe3 at low temperature (eq 9) and was not isolated cleanly (TTP)SnCl2 + 2LiCH2-CMe3 → (TTP)Sn(3CH2CMe3)2 + 2LiCl \hspace{1cm} (9)

due to decomposition. The A2B2 splitting pattern for the tolyl protons in the 1H 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, Me2SiCH2), etc.\textsuperscript{9,26}

The products produced from the reaction between (TTP)-Li2(THF)2 and 1 equiv of Me2SnBr2 are solvent dependent. In toluene, the product is cis-(TTP)SnMe2 (8) (eq 10). This result (TTP)Li2(THF)2 + Me2SnBr2 \text{to-toluene} \rightarrow \text{cis-}(TTP)SnMe2 + 2LiBr + 2THF \hspace{1cm} (10)
The acetylide complexes (TTP)Sn(C≡CPh)2 (10) and (TTP)-Sn(C≡CSiMe3)2 (11) were isolated via the reaction of (TTP)-SnCl2 with the corresponding alkynyllithium salt (eq 12). The

$$(TTP)SnCl_2 + 2LiR \rightarrow (TTP)Sn(R)_2 + 2LiCl \quad (12)$$

10, 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

$$(TTP)Sn(C≡CPh)_2 + MeOH \rightarrow 10$$

$$(TTP)Sn(C≡CPh)(OMe) + PhC≡CH \quad (13)$$

$$(TTP)Sn(C≡CPh)(OMe) + MeOH \rightarrow 12$$

$$(TTP)Sn(OMe)_2 + PhC≡CH \quad (14)$$

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 C6D6 in a NMR tube at ambient temperature, no reaction was detected after 23 h via 1H NMR spectroscopy (reaction 16). The substitution chemistry described here reveals

$$(TTP)Sn(C≡CPh)_2 + 2,3,5,6-C_6F_4HNH_2 \rightarrow 10 \quad (16)$$

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

$$NR_1R_2 < C≡CPh, C≡CSiMe_3 < OMe$$

This trend correlates well with the decreased basicity of NH2- (or NR1R2-) > HC≡C- (or RC≡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.

**X-ray Crystal Structure of 10.** In the crystal structure of 10, each unit cell contains two molecules in the space group $P2_1_2_1_2$. The coordination geometry of (TTP)Sn(C≡CPh)2 is shown in Figure 1. This molecule has a pseudo-octahedral 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)F2 2.056(7) and 2.071(6) Å, Sn–N in Sn(TPP)(NO3)2 2.075(5) and 2.080(5) Å,2,3 but are smaller than those in trans-Sn(TPP)-Ph2(CH2Cl2) (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)Ph2(CH2Cl2).11 The Sn–C distance in 10 is also comparable to the Sn–C distances in other tin complexes, such as [Me2Sn(NH2)2][N(SO2Me)2] (Sn–C 2.124(2)–2.117(2) Å),28 [C6H5]2SnCrH2(CF3)$_2$ (Sn–C 2.145(8)–2.233(7) Å),29 [(CH3)2SnOC(CF3)$_2$]2CF4 (Sn–C 2.097(19)–2.134(23) Å)30 and (CH3)$_2$SnN(SO2CH3)$_2$]2 (Sn–C 2.101(3)–2.108(3) Å),31 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


of 1.187(7) Å in trans-[N(H3)Ru(C==CPh)(Ph2P(CH2)2PPh2)2]-PF6.32 Very little, if any, \(\pi\)-bonding exists between the acetylide ligands and Sn metal center. The angles of Sn(1)-N(2A)-C(25) and Sn(1)-N(2)-C(25) 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(NPh2)2, and (TTP)Sn(o-C6H4(NH)2), and dialkyltin porphyrins, including (TTP)Sn(C==CPh)2 and (TTP)Sn(C==CSiMe3)2, can be isolated via the reactions of (TTP)SnCl2 with related lithium amide and alkylithium salts. This is a new route for the synthesis robust dialkyltin porphyrins. With the reaction of (TTP)SnCl2 with ZnEt2 and the reactions of Li2(TTP)(THF)2 with Me2SnBr2 in different solvents at low temperatures, labile (TTP)SnEt2, cis-(TTP)SnMe2, and trans-(TTP)SnMeBr could be synthesized. The X-ray structure of (TTP)Sn(C==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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