

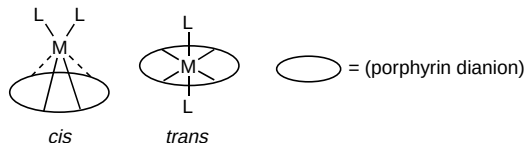
Stereochemical Control in Metalloporphyrin Chemistry: Synthesis and Characterization of *cis*- and *trans*-Sn(porphyrin)Ph₂

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Received March 27, 1996

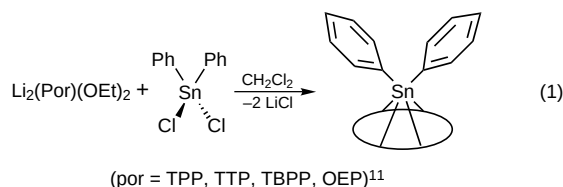
In metalloporphyrin chemistry, *cis* versus *trans* coordination geometries are generally assumed to be controlled by the nature of the metal ion, with the *trans* (or axial) arrangement being



by far the most common by virtue of the fact that most transition and main group elements fit comfortably in the N₄ plane of the porphyrin ligand. Large ions, such as those early in the transition series (e.g. Zr, Hf, Nb, Ta), sit out of the plane of the ring, thereby directing additional ligands to *cis* coordination sites.¹ Here we report an unusual example of stereochemical control in Sn(IV) porphyrin chemistry exerted not by the metal ion but by the choice of synthetic route.

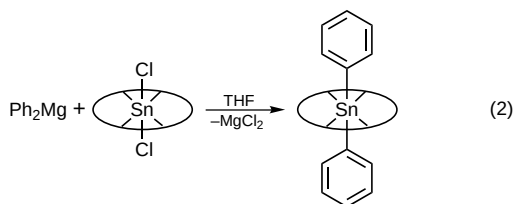
In spite of the fact that the covalent radius of Sn is rather large, being roughly in between that of Ti and Zr, all reported derivatives of general formula Sn(por)L₂ (L = e.g. F, Cl, OMe, OH) show *trans* geometries.^{2,3} Tin porphyrin dialkyls were first reported by Pommier^{4–6} but could not be isolated because of their photoactivity and O₂ sensitivity. Kadish recently prepared the first porphyrin complexes containing a stable tin–carbon bond by oxidative addition of MeI to Sn(II)(Por).⁷ There are, however, many organometallic derivatives of most of the other metalloid porphyrins, including germanium, silicon, and all of the Group 13 metals. The fact that there are so few tin(IV) porphyrin organometallic complexes is surprising, particularly in view of the potential biological interest (e.g. antitumor activity) of such compounds.^{7–9}

We recently described a low-temperature route for the preparation of *cis*-Zr(por)Cl₂ using Li₂(por) salts in combination with ZrCl₄(THF)₂.¹⁰ Reasoning that if the reaction conditions were mild enough to suppress ligand exchange we might be able to isolate the unknown *cis*-ligated species, we investigated the reaction of Li₂(por) (as DME or OEt₂ solvates) with SnCl₂-Ph₂ in dichloromethane, as shown in eq 1. For each porphyrin studied, the purple, crystalline *cis* isomer was obtained in yields



of approximately 70–80% after recrystallization.¹² These compounds are light sensitive and thermally stable and can be stored in a dry box (wrapped in foil) for months without decomposition. In solution, ¹H and ¹³C NMR spectroscopy indicated the absence of mirror symmetry in the porphyrin plane, suggesting *cis* geometries, and in the solid state, X-ray crystallography confirmed this stereochemistry for the TBPP derivative (Figure 1).

For comparison, the *trans* isomers were readily prepared from the known *trans*-Sn(por)Cl₂¹³ and diphenylmagnesium (eq 2).



Due to their high symmetry, the compounds are readily identified as the *trans* derivatives by NMR spectroscopy. The *trans* geometry of Sn(TPP)Ph₂ was further confirmed by X-ray crystallography (see Figure 2).

For the *cis* derivatives, the *ortho* H's of the coordinated phenyl group appear as a doublet, with ¹¹⁹Sn satellites (²J_{Sn–H} = ca. 95 Hz) at between 3.0 and 3.4 ppm. This chemical shift is almost identical to that seen in the diaryl zirconium porphyrin Zr(OEP)(C₆H₄Bu')₂.¹⁰ This resonance occurs at 0.8 ppm in the *trans* species, suggesting a closer proximity of these H's to the center of the anisotropic porphyrin ring.¹⁴ The lack of mirror symmetry in the porphyrin ring in the *cis*-ligated tin porphyrin complexes is shown by the nonequivalence of the *ortho* protons of the *meso* aryl on the ring, observed at room temperature as two broad resonances, in contrast to the sharp doublet in the analogous *trans*-diphenyl tin porphyrins. In the related OEP derivative, the same phenomenon renders the methylene protons diastereotopic. Both sets of isomers show normal-type UV–vis spectra.¹⁵

X-ray quality crystals of Sn(TBPP)Ph₂(C₆H₅Cl)_{3.5} were obtained from a mixture of chlorobenzene and hexanes.¹⁶ The structure shows the tin atom to be well out of the plane of the

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(11) Abbreviations: TPP is the dianion of *meso*-tetraphenylporphyrin; TTP is the dianion of *meso*-tetra-*p*-tolylporphyrin; TBPP is the dianion of *meso*-tetra-*p*-tert-butylphenylporphyrin; OEP is the dianion of 2,3,7,8,12,13,17,18-octaethylporphyrin.

(12) Selected characterization data for new compounds. *cis*-(TTP)-SnPh₂: ¹H NMR (300 MHz, CDCl₃) δ 2.71 (s, 12), 3.36 (d, 4), 6.00 (m, 4), 6.22 (t, 2), 7.19 (d, tol), 7.24 (d, tol), 7.45 (d, 8), 8.03 (d, 8), 8.89 (s, 8). UV/vis (C₆H₆) 340, 442, 516, 552, 582, 632 nm. *cis*-(TBPP)SnPh₂: ¹H NMR (300 MHz, CDCl₃) δ 1.60 (s, 36), 2.52 (s, 3, tol), 3.41 (d, 4), 6.06 (m, 4), 6.23 (t, 2), 7.20 (d, 2, tol), 7.24 (d, 2, tol), 7.72 (m, 8), 7.8–8.2 (br m, 8), 9.01 (s, 8). UV/vis (CH₂Cl₂) 340, 440, 486, 546, 579, 631 nm. *trans*-(TTP)SnPh₂: ¹H NMR (300 MHz, CDCl₃) δ 0.84 (d, 4), 2.71 (s, 12), 5.06 (m, 4), 5.48 (t, 2), 7.19 (d, tol), 7.57 (d, 8), 8.03 (d, 8), 8.11 (d, 8), 9.06 (s, 8). UV/vis (C₆H₆) 356, 450, 600, 646 nm. *trans*-(TPP)SnPh₂: ¹H NMR (300 MHz, CDCl₃) δ 0.85 (d, 4), 5.03 (m, 4), 5.29 (s, 2, CH₂Cl₂), 5.50 (t, 2), 7.79 (m, 12), 8.22 (d, 8), 8.99 (s, 8). UV/vis (C₆H₆) 350, 448, 602, 646 nm. *trans*-(TTP)Sn(Ph)Cl: ¹H NMR (300 MHz, CDCl₃) δ 1.42 (d, 2), 2.73 (s, 12), 5.30 (m, 2), 5.73 (t, 1), 7.60 (m, 8), 8.09 (dd, 4), 8.26 (dd, 4), 9.13 (s, 8). UV/vis (C₆H₆) 354, 420, 442, 570, 622 nm. Full details are provided as supporting information.

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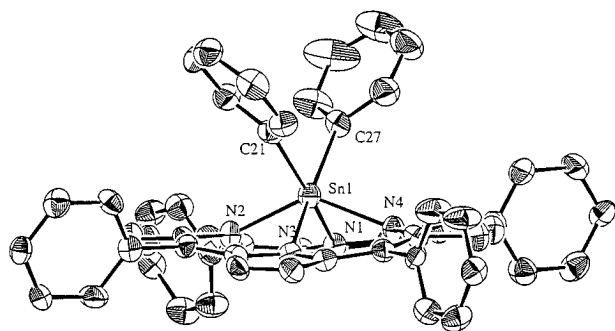


Figure 1. Shown is an ORTEP view of (TBPP)SnPh₂, with ellipsoids drawn at 50% probability and the hydrogens and *tert*-butyl groups omitted for clarity. Sn–N bond distances: 2.367(6), 2.171(5), 2.341(6), and 2.183(6) Å. Sn–C bond distances: 2.210(7) and 2.193(7) Å. C–Sn–C angle: 89.7(3)°.

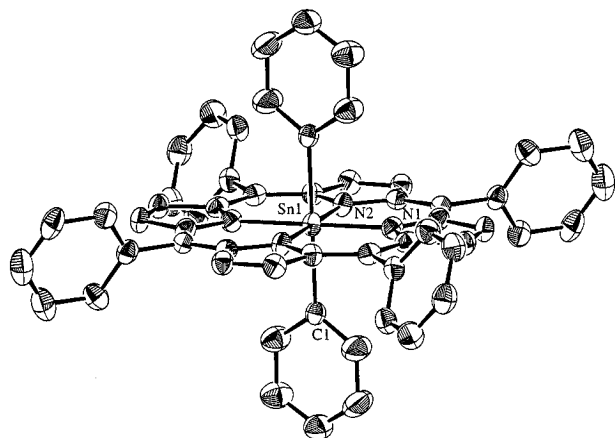


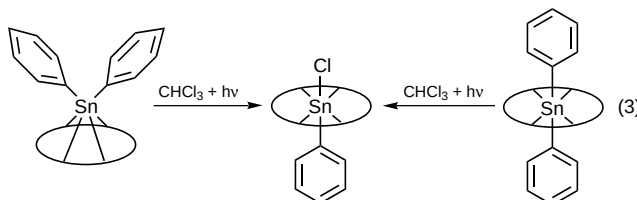
Figure 2. Shown is an ORTEP view (TPP)SnPh₂·(CH₂Cl₂) (molecule 1) with ellipsoids drawn at 50% probability and hydrogens omitted for clarity. Sn–N bond distance (av): 2.134(4) Å. Sn–C bond distances: 2.196(4) and 2.212(4) Å.

porphyrin (1.11 Å out of the mean plane of the porphyrin), with a phenyl–tin–phenyl angle of 89.7°. The porphyrin ring is highly distorted (both ruffled and domed), and the Sn–N bond distances show two short and two long interactions, perhaps due to steric repulsion between the phenyl rings and the pyrrole rings closest to them.

The typical, in-plane, octahedral coordination geometry of the *trans* derivatives was confirmed by the crystal structure of *trans*-Sn(TPP)Ph₂(CH₂Cl₂), obtained from diffusion of ether into

a methylene chloride solution of the compound.¹⁷ The core of the porphyrin macrocycle is slightly expanded, with the Sn–N bonds being somewhat longer than in previously reported tin(IV) porphyrin derivatives.

Exposure of either isomer to light in CHCl₃ results in formation of *trans*-Sn(Por)Ph(Cl) (eq 3). This reaction is clean



for the *trans* derivative; however, for the *cis* the ¹H NMR spectrum indicates the formation of additional products in which the porphyrin ring symmetry is disrupted. Decomposition products of this type are also observed in the light sensitive dialkyl zirconium and trialkyl tantalum porphyrins, but we have been unable to isolate or characterize any of these species.¹⁸ Facile cleavage of one M–R bond is common in Group 14 metallocporphyrins,^{4,6,19–21} and analogous chemistry of diphenyl germanium porphyrin has been reported.^{20,21}

In summary, using a new low-temperature synthetic route, we have been able to prepare novel *cis*-Sn(Por)Ph₂ isomers, in which the resulting stereochemistry is controlled not by the nature of the central metal ion, but by choice of synthetic method. This is an unusual system in that both *cis* and *trans* metallocporphyrin geometries are accessible and stable.

Acknowledgment. We thank the donors of the Petroleum Research Fund administered by the American Chemical Society for partial funding, the Sloan Foundation for the award of a fellowship to J.A., and the National Physical Sciences Consortium for a fellowship to D.Y.D.

Supporting Information Available: Experimental details and characterization data for new compounds and details of structure determinations, including tables of crystal and data collection parameters, anisotropic thermal parameters, positional parameters, and ORTEP representations (22 pages). See any current masthead page for ordering and Internet access instructions.

JA961007C

(17) Crystal data for (TPP)SnPh₂(CH₂Cl₂): C₅₇H₄₀N₄Cl₂Sn, mw = 970.57, space group *P*1 (No. 2) with *a* = 10.0503(3) Å, *b* = 12.5071(4) Å, *c* = 18.6408(7) Å, α = 75.239(1)°, β = 85.026(1)°, γ = 81.483(1)°, *V* = 2237.9(1) Å³, *d*_{calc} = 1.440 g cm^{−3}, and *Z* = 2. Data were collected on a Siemens SMART diffractometer at −105 °C with Mo Kα (λ = 0.71069 Å). A 2θ range from 3–46.5° gave 6204 unique reflections. The structure was solved by direct methods and refined by least squares and Fourier techniques using 588 variables against 5143 data for which *I* > 3σ(*I*), to give *R* = 0.040, *R*_w = 0.052, and GOF = 2.51.

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(16) Crystal data for (TBPP)SnPh₂(PhCl)_{3.5}: C₉₇H_{100.5}N₄Cl_{3.5}Sn, mw = 1565.16, space group *P*2₁/*n* (No. 14) with *a* = 17.0864(4) Å, *b* = 17.9988(4) Å, *c* = 25.6002(4) Å, β = 93.599(1)°, *V* = 7857.4(2) Å³, *d*_{calc} = 1.323 g cm^{−3}, and *Z* = 4. Data were collected on a Siemens SMART diffractometer at −130 °C with Mo Kα (λ = 0.71069 Å). A 2θ range from 3–46.5° gave 11 589 unique reflections. The structure was solved by direct methods and refined by least squares and Fourier techniques using 870 variables against 7058 data for which *I* > 3σ(*I*), to give *R* = 0.064, *R*_w = 0.071, and GOF = 2.63.