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Synthesis and Molecular Structure of (TTP)Ti(1,2-η^2-PhC≡C−C≡CPh)

Jinyuan Chen, Ilia A. Guzei, and L. Keith Woo*

Department of Chemistry, Iowa State University
Ames, Iowa 50011-3111

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Introduction

Titanium porphyrin complexes of the general formula Ti(por)L_1L_2 or Ti(por)L_1 (por = general porphyrin dianion; L_1, L_2 = halide, NR, NHR, NR_2, OR, O, O_2, S, S_2, RC≡CR, THF, RN═NR, etc.)[1−8] are well-known. However, metalloporphyrin complexes with titanium−carbon σ-bonded axial ligands are still rare. The only reported examples are monoalkyl metalloporphyrin complexes, Ti(TPP)R (TPP = *meso*-5,10,15,20-tetraphenylporphyrinato dianion; R = C_6H_5, *o*-$CH_3C_6H_4$, and $CH_2C_6H_5$).[9] In contrast, Zr(IV) and Hf(IV) porphyrin complexes with two alkyl ligands are well characterized.[1,10] In this work, synthesis of dialkyl titanium metalloporphyrin complexes was attempted.

Experimental Section

General Methods. The synthesis and handling of air-sensitive porphyrin complexes and treatment of solvents were performed as described previously.[11] Literature procedures were used to synthesize (TTP)$TiCl_2$,[2] (TTP)TiCl,[2] and (TTP)Ti(η^2-EtC≡CEt).[6] Lithium phenylacetylide was synthesized by the reaction of phenylacetylene with *n*-butyllithium (1.6 M in hexane) in Et_2O. LiC≡CSi$(CH_3)_3$ was prepared from $(CH_3)_3$SiC≡CH and BuLi in hexane. Other chemicals were reagent grade and used without further purification.

Proton NMR spectra were obtained on a Varian VXR-300 spectrometer (300 MHz). UV−visible spectra were obtained using a Hewlett-Packard HP 8452A diode-array spectrophotometer. X-ray crystallographic analysis was performed on a Bruker CCD-1000 diffractometer. MS analysis was performed on a Finnigan TSQ 700 mass spectrometer.

(TTP)Ti(1,2-η^2-PhC≡C−C≡CPh), 1. Method A. To a stirred solution of (TTP)$TiCl_2$ (0.043 g, 0.055 mmol) in approximately 12 mL of a toluene:THF mixture (10:1 v:v) at −25 °C was added 0.014 g of PhC≡CLi (0.13 mmol). The solution was then kept at −25 °C in a glovebox. After 20 h, the solution was taken to dryness in vacuo at ambient temperature. The residue was then redissolved in ca. 2 mL of toluene and filtered off. The filtrate was layered with 4−5 mL of hexane and cooled to −25 °C. After 1 day, a dark blue precipitate was isolated by filtration, washed with hexanes, and dried in vacuo (17 mg, 34% yield). ^{1}H NMR (C_6D_6, ppm): 9.14 (s, 8H, β-H), 8.12 (d, 4H, −C_6H_4-Me), 7.99 (d, 4H, −C_6H_4Me), 7.25 (pseudo t, 8H, −C_6H_4Me), 6.82 (m, 5H, −C_6H_5), 6.40 (m, 3H, −C_6H_5), 5.14 (dd, 2H, −C_6H_5), 2.38 (s, 12H, −C_6H_4*Me*). UV−vis (toluene): 426 (Soret), and 551 nm.

Method B. To a stirred solution of (TTP)TiCl (0.146 g, 0.194 mmol) and 1,4-diphenylbutadiyne (0.153 g, 0.758 mmol) in ca. 18 mL of toluene was added dropwise 0.218 mL of $NaBEt_3H$ solution (1.0 M in toluene) at ambient temperature. After stirring for 24 h, the solution was filtered and the filtrate was concentrated to 3 mL and mixed with 5 mL of hexanes. The solution was then cooled to −25 °C to deposit dark blue microcrystals. The product was then isolated by filtration, washed with hexanes, and dried in vacuo (80 mg, 44%). The ^{1}H NMR and UV−vis spectra were identical to those reported in method A.

Method C. After dissolving 0.004 g of (TTP)Ti(η^2-EtC≡CEt) (0.005 mmol) into 0.7 mL of C_6D_6 in an NMR tube fitted with a high-vacuum Teflon stopcock, 0.004 g of 1,4-diphenylbutadiyne (0.02 mmol) was added to the solution at ambient temperature. After 1 h, (TTP)Ti(η^2-EtC≡CEt) was completely converted to (TTP)Ti(PhC≡CC≡CPh) as monitored by ^{1}H NMR. The ^{1}H NMR of **1** in C_6D_6 was identical to the data reported in method A. ^{1}H NMR of free EtC≡CEt (C_6D_6, ppm): 2.03 (m, 4H), 0.99 (t, 6H), identical to the NMR spectrum of authentic compound.

(TTP)Ti(η^2-TMSC≡CC≡CTMS), 2. To a stirred solution of (TTP)$TiCl_2$ (0.033 g, 0.041 mmol) in ca. 10 mL of toluene/THF(10:1) at −25 °C was added TMSC≡CLi (0.012 g, 0.12 mmol). After 22 h at −25 °C, the solution was taken to dryness in vacuo. The ^{1}H NMR spectrum of the residue showed that (TTP)Ti(η^2-TMSC≡CC≡CTMS) was the main product. Further purification by following a similar route to purify **1** failed due to the oxidation of **2** in the glovebox to form (TTP)Ti═O. ^{1}H NMR of (TTP)Ti(η^2-TMSC≡CC≡CTMS) (C_6D_6, ppm): 9.07 (s, 8H, β-H), 8.34 (d, 4H, −C_6H_4Me), 7.95 (d, 4H, −C_6H_4-Me), 7.36 (d, 4H, −C_6H_4Me), 7.26 (d, 4H, −C_6H_4Me), 2.40 (s, 12H, −C_6H_4*Me*), −0.15 (s, 9H, −Si$(CH_3)_3$), −1.22 (s, 9H, −Si$(CH_3)_3$).

Reaction of (TTP)Ti(η^2-PhC≡CC≡CPh) with Air. After ca. 3 mg of **1** was dissolved into 0.7 mL of C_6D_6 at ambient temperature, the solution was opened in the air for approximately 1 h. The ^{1}H NMR spectrum showed that **1** was cleanly converted to (TTP)Ti═O and PhC≡CC≡CPh. The mass spectrum (EI) of the solution showed a *m*/*e* peak at 202.1, corresponding to the molecular weight of 1,4-diphenylbutadiyne (MW: 202.261). ^{1}H NMR spectrum of PhC≡CC≡CPh (C_6D_6, ppm): 7.34 (dd, 4H), 6.87 (m, 6H), identical to that of the authentic compound.

Reaction of (TTP)Ti(η^2-PhC≡CC≡CPh) with Pyridine. After dissolving ca. 4 mg of **1** into 0.7 mL of C_6D_6 at ambient temperature, excess pyridine was add to the solution. A ^{1}H NMR spectrum taken immediately showed that **1** was completely converted to (TTP)Ti$(py)_2$ and PhC≡CC≡CPh. ^{1}H NMR of (TTP)Ti$(py)_2$ (C_6D_6, ppm): 22.95 (s, 4H, *o-py*), 13.78 (s, 4H, *m-py*), 6.26 (d, 8H, −C_6H_4Me), 4.30 (d, 8H, −C_6H_4Me), 1.61 (s, 12H, −C_6H_4Me), −11.79 (s, 8H, β-H), experimentally similar to the data reported in the literature.[12]

X-ray Structure Determination of 1. Selected crystallographic data for the crystal structure determination of complex **1** are shown in Table 1. The crystal evaluation and data collection were performed on a Bruker CCD-1000 diffractometer.

The systematic absences in the diffraction data were uniquely consistent for the space group $P2_1/c$, which yielded chemically reasonable and computationally stable results of refinement.[13] The structure was solved using direct methods, completed by subsequent difference Fourier synthesis and refined by full-matrix least-squares procedures. All non-hydrogen atoms were refined with anisotropic

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(13) All software and sources of the scattering factors are contained in the SHELXTL (version 5.1) program library (G. Sheldrick, Bruker Analytical X-Ray Systems, Madison, WI).

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Table 1. Selected Crystallographic Data and Structure Refinement for the Structure Determination of (TTP)Ti(η^2-PhC≡C−C≡CPh)

empirical formula	$C_{64}H_{48}N_4Ti$
fw	920.96
temp, K	173(2)
λ, Å	0.71073
space group	$P2_1/c$
a, Å	14.1665(7)
b, Å	24.7743(12)
c, Å	16.2716(8)
β, deg	97.994(1)
vol, Å^3	5655.3(5)
Z	4
density (calcd), Mg/m^3	1.082
abs coeff, μ	0.191
goodness-of-fit on F^2	1.037
final *R* Indices [$I > 2\sigma(I)$]^a	R1 = 0.0634, wR2 = 0.1535

^{a} $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{0.5}$.

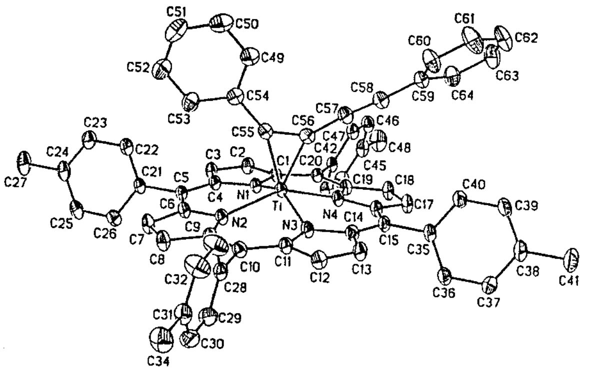

Figure 1. Molcular structure of (TTP)Ti(η^2-PhC≡C−C≡CPh). Thermal ellipsoids are drawn at the 30% probability level.

displacement coefficients. All hydrogen atoms were treated as idealized contributions. The refinement of the structure of **1** revealed the presence of severely disordered solvent molecules. The SQUEEZE filter of the program PLATON[14] was applied to identify and account for six solvent molecules of toluene present in the unit cell along with four molecules of the complex.

A significant amount of time was invested in identifying and refining these solvates as toluene molecules. Bond length restraints were applied to model these molecules, but the resulting isotropic displacement coefficients suggested that the molecules were mobile. In addition, the refinement was computationally unstable. Option SQUEEZE of program PLATON was used to correct the diffraction data for diffuse scattering effects and to identify the solvate molecules. PLATON calculated the upper limit of volume that can be occupied by the solvent to be 1182.7 Å^3, or 20.9% of the unit cell volume. The program calculated 312 electrons in the unit cell for the diffuse species. This approximately corresponds to six toluene molecules in the unit cell (300 electrons). No data are given for the diffusely scattering species (solvent molecules).

Results and Discussion

(TTP)Ti(1,2-η^2-PhC≡CC≡CPh), 1. Lithium phenylacetylide was successfully used to synthesize robust tin metalloporphyrin complexes containing one or two metal−carbon σ-bonded axial ligands.[11] Because Sn and Ti have similar valence states and sizes, analogous Ti complexes were expected. However, the desired target complex was not obtained. When (TTP)TiCl$_2$ was treated with more than 2 equiv of LiC≡CPh in toluene/THF at low temperature (−25 °C), (TTP)TiCl$_2$ was reduced to form a Ti(II) complex. Two phenylacetylide anions were concomitantly oxidized and coupled to form a π-bonded 1,4-diphenylbutadiyne (eq 1).

$$\mathrm{(TTP)TiCl_2 + 2PhC{\equiv}CLi \xrightarrow[-25\ ^\circ C]{tol/THF} \underset{\mathbf{1}}{(TTP)Ti(\eta^2\text{-}PhC{\equiv}CC{\equiv}CPh)} + 2LiCl} \quad (1)$$

To verify the formulation of this product, two independent routes to synthesize complex **1** were used. The reaction of (TTP)Ti(η^2-EtC≡CEt) with excess PhC≡CC≡CPh resulted in ligand exchange (eq 2). An alternate route was homogeneous reduction of Ti(III) with NaBEt$_3$H in the presence of PhC≡CC≡CPh (reaction 3).

$$\mathrm{(TTP)Ti(\eta^2\text{-}EtC{\equiv}CEt) + PhC{\equiv}CC{\equiv}CPh \rightarrow (TTP)Ti(\eta^2\text{-}PhC{\equiv}CC{\equiv}CPh) + EtC{\equiv}CEt} \quad (2)$$

$$\mathrm{(TTP)TiCl + NaBEt_3H + PhC{\equiv}CC{\equiv}CPh \rightarrow (TTP)Ti(\eta^2\text{-}PhC{\equiv}CC{\equiv}CPh)} \quad (3)$$

The five-coordinate geometry of complex **1** was shown by the nonequivalent ortho protons of the tolyl groups on the macrocycle (8.12 (d) and 7.99 (d) ppm). The singlet due to the eight β-pyrrole protons indicated that the π-bound ligand PhC≡CC≡CPh rotates rapidly about the axial position. The phenyl substituents of the bound diyne ligand are clearly inequivalent. The protons of one phenyl group appear at 6.82 ppm (m, 5H), while the other phenyl group gives rise to signals at 6.40 (m, 3H) and 5.14 (dd, 2H) ppm. These data are consistent with a 1,2-η^2 coordination mode of 1,4-diphenylbutadiyne. An X-ray molecular structure of complex **1** verified this coordination geometry (vide infra).

Complex **1** was easily oxidized in air to form (TTP)Ti=O. The pyridine exchange reaction of **1** to form (TTP)Ti(py)$_2$ (eq 4) also indicated that the ligand binding strength of PhC≡CC≡CPh to (TTP)Ti(II) is similar to that of PhC≡CPh.

$$\mathrm{(TTP)Ti(\eta^2\text{-}PhC{\equiv}CC{\equiv}CPh) + 2\ pyridine \rightarrow (TTP)Ti(py)_2 + PhC{\equiv}CC{\equiv}CPh} \quad (4)$$

A recent article reported that the treatment of (por)ZrCl$_2$ with excess LiC≡CR produced (por)Zr(η^1-C≡CR)$_3$Li(THF) (por = octaethylporphyrinato or tetraphenylporphyrinato dianion; R = Ph, SiMe$_3$).[15] The greater size and electropositivity of Zr rationalizes this difference in chemistry.

(TTP)Ti(η^2-TMSC≡CC≡CTMS), 2. Complex **2** was synthesized from (TTP)TiCl$_2$ and excess TMSC≡CLi in toluene/THF(10:1) at −25 °C. The ^{1}H NMR spectrum of complex **2** indicated that its coordination geometry is quite similar to that of complex **1**. Complex **2** failed to be purified, as the workup process always resulted in partial decomposition to (TTP)Ti=O.

The reactivity differences between **1** and **2** are possibly due to the π-acceptor differences between 1,4-diphenylbutadiyne and TMSC≡CC≡CTMS. A related study[16] showed that the mode of reaction of titanocene “Cp$_2$Ti” with disubstituted butadiynes RC≡CC≡CR depended strongly on the nature of the substituent. For R = SiMe$_3$ the starting butadiyne was cleaved by titanocene to yield the dinuclear complex [Cp$_2$Ti(C≡CSiMe$_3$)]$_2$. In contrast,

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Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) in Complex **1**

Ti−C(56)	2.018(3)	Ti−C(55)	2.019(3)
Ti−N(1)	2.1003(19)	Ti−N(3)	2.103(2)
Ti−N(4)	2.109(2)	Ti−N(2)	2.122(2)
C(54)−C(55)	1.462(4)	C(55)−C(56)	1.316(4)
C(56)−C(57)	1.396(4)	C(57)−C(58)	1.210(4)
C(58)−C(59)	1.428(4)	C(55)−Ti−N(1)	99.11(9)
C(56)−Ti−C(55)	38.06(10)	C(55)−Ti−N(3)	111.48(9)
C(56)−Ti−N(1)	116.61(9)	C(56)−Ti−N(4)	86.37(10)
C(56)−Ti−N(3)	92.98(9)	N(1)−Ti−N(4)	85.02(7)
C(55)−Ti−N(4)	119.55(10)	C(56)−Ti−N(2)	125.39(10)
C(55)−Ti−N(2)	92.90(9)	C(56)−C(55)−C(54)	134.1(3)
C(56)−C(55)−Ti	70.91(17)	C(54)−C(55)−Ti	154.9(2)
C(55)−C(56)−C(57)	143.5(3)	C(55)−C(56)−Ti	71.03(17)
C(57)−C(56)−Ti	145.5(2)	C(58)−C(57)−C(56)	175.1(3)

for R = Ph only a dinuclear complex with a central 1,4-disubstituted μ-η(1,3),η(2,4)-*trans*,*trans*-butadiene unit (“zigzag-butadiyne”) between the two titanium centers was formed. Such differences are likely due to the electronic effect of the substituents on the diyne.[15]

X-ray Structure of 1. The coordination geometry of (TTP)-Ti(η^2-PhC≡CC≡CPh) is shown in Figure 1. Only one C≡C bond of the axial ligand is bound to Ti in a 1,2-η^2 coordination mode. Selected bond lengths and bond angles of this molecule are listed in Table 2. The Ti−N bond distances range from 2.1003(19) to 2.109(2) Å, similar to the Ti−N bond distances [2.094(7)−2.099(7) Å] in (OEP)Ti(η^2-PhC≡CPh).[6] The Ti−C distances are 2.018(3) and 2.019(3) Å and are also quite similar to those in (OEP)Ti(η^2-PhC≡CPh) [2.016(5) and 2.015(5) Å].[6] In complex **1**, the C55−C56 bond distance is 1.316(4) Å. The uncomplexed C≡C bond distance is 1.210(4) Å (C57−C58). In (OEP)Ti(η^2-PhC≡CPh), the C≡C bond distance is 1.30(1) Å. As in (OEP)Ti(η^2-PhC≡CPh), the butadiyne ligand in complex **1** can be regarded as a 4e$^-$ donor to the titanium center. The bond angles of C55−C56−C57 and C56−C57−C58 are 143.5(3)° and 175.1(3)°, respectively.

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Supporting Information Available: An X-ray crystallographic file in CIF format for the structure determination of (TTP)Ti(1,2-η^2-PhC≡C−C≡CPh). This material is available free of charge via the Internet at http://pubs.acs.org.

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